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(54) Title: LITHIUM-BASED ELECTROCHEMICALLY ACTIVE MATERIALS AND PREPARATION THEREOF

(57) Abstract: The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium.

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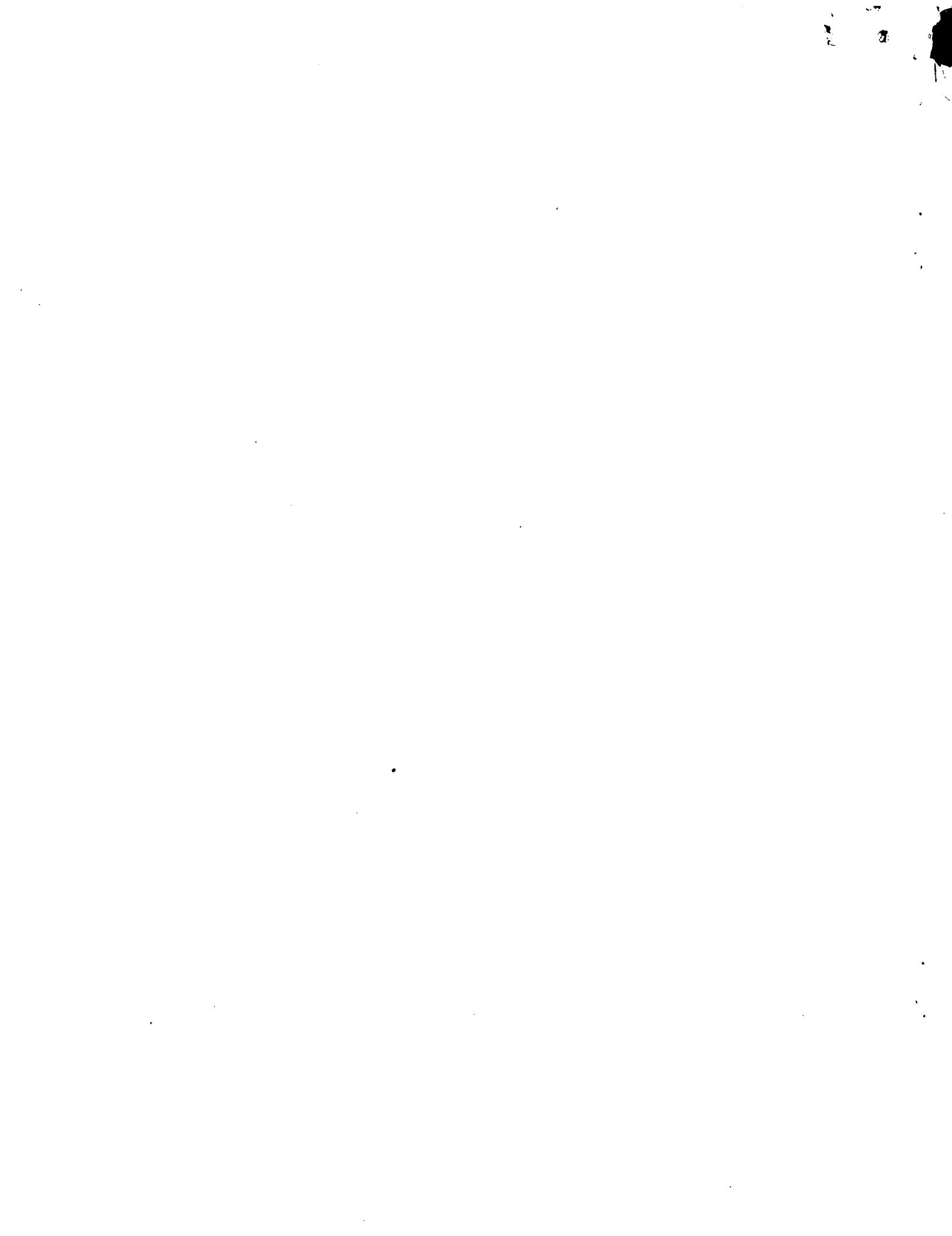
# LITHIUM-BASED ELECTROCHEMICALLY ACTIVE MATERIALS AND PREPARATION THEREOF

## Field of the Invention

5       This invention relates to improved materials
usable as electrode active materials and to their
preparation.

## Background of the Invention

        Lithium batteries are prepared from one or more
10      lithium electrochemical cells containing
electrochemically active (electroactive) materials. Such
cells typically include an anode (negative electrode), a
cathode (positive electrode), and an electrolyte
interposed between spaced apart positive and negative
15      electrodes. Batteries with anodes of metallic lithium
and containing metal chalcogenide cathode active material
are known. The electrolyte typically comprises a salt of
lithium dissolved in one or more solvents, typically
nonaqueous (aprotic) organic solvents. Other
20      electrolytes are solid electrolytes typically called
polymeric matrixes that contain an ionic conductive
medium, typically a metallic powder or salt, in
combination with a polymer that itself may be ionically
conductive which is electrically insulating. By
25      convention, during discharge of the cell, the negative
electrode of the cell is defined as the anode. Cells
having a metallic lithium anode and metal chalcogenide
cathode are charged in an initial condition. During
discharge, lithium ions from the metallic anode pass
30      through the liquid electrolyte to the electrochemical

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active (electroactive) material of the cathode whereupon
they release electrical energy to an external circuit.

It has recently been suggested to replace the
lithium metal anode with an insertion anode, such as a
5    lithium metal chalcogenide or lithium metal oxide.
Carbon anodes, such as coke and graphite, are also
insertion materials.  Such negative electrodes are used
with lithium- containing insertion cathodes, in order to
form an electroactive couple in a cell.  Such cells, in
10   an initial condition, are not charged.  In order to be
used to deliver electrochemical energy, such cells must
be charged in order to transfer lithium to the anode from
the lithium- containing cathode.  During discharge the
lithium is transferred from the anode back to the
15   cathode.  During a subsequent recharge, the lithium is
transferred back to the anode where it re-inserts.  Upon
subsequent charge and discharge, the lithium ions ($Li^+$)
are transported between the electrodes.  Such
rechargeable batteries, having no free metallic species
20   are called rechargeable ion batteries or rocking chair
batteries.  See U.S. Patent Nos. 5,418,090; 4,464,447;
4,194,062; and 5,130,211.

Preferred positive electrode active materials
include $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$.  The cobalt compounds
25   are relatively expensive and the nickel compounds are
difficult to synthesize.  A relatively economical
positive electrode is $LiMn_2O_4$, for which methods of
synthesis are known.  The lithium cobalt oxide ($LiCoO_2$),
the lithium manganese oxide ($LiMn_2O_4$), and the lithium
30   nickel oxide ($LiNiO_2$) all have a common disadvantage in
that the charge capacity of a cell comprising such
cathodes suffers a significant loss in capacity.  That

is, the initial capacity available (amp hours/gram) from $LiMn_2O_4$, $LiNiO_2$, and $LiCoO_2$ is less than the theoretical capacity because significantly less than 1 atomic unit of lithium engages in the electrochemical reaction. Such an

5    initial capacity value is significantly diminished during the first cycle operation and such capacity further diminishes on every successive cycle of operation. For $LiNiO_2$ and $LiCoO_2$ only about 0.5 atomic units of lithium is reversibly cycled during cell operation. Many

10   attempts have been made to reduce capacity fading, for example, as described in U.S. Patent No. 4,828,834 by Nagaura et al. However, the presently known and commonly used, alkali transition metal oxide compounds suffer from relatively low capacity. Therefore, there remains the

15   difficulty of obtaining a lithium-containing electrode material having acceptable capacity without disadvantage of significant capacity loss when used in a cell.

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## Summary of the Invention

The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium. Accordingly, the invention provides a rechargeable lithium battery which comprises an electrolyte; a first electrode having a compatible active material; and a second electrode comprising the novel materials. In one aspect, the novel materials are lithium-mixed metal phosphates which preferably used as a positive electrode active material, reversibly cycle lithium ions with the compatible negative electrode active material. Desirably, the lithium-mixed metal phosphate is represented by the nominal general formula $Li_aMI_bMII_c(PO_4)_d$. Such compounds include $Li_1MI_aMII_bPO_4$ and $Li_3MI_aMII_b(PO_4)_3$; therefore, in an initial condition $0 \le a \le 1$ or $0 \le a \le 3$, respectively. During cycling, x quantity of lithium is released where $0 \le x \le a$. In the general formula, the sum of b plus c is up to about 2. Specific examples are $Li_1MI_{1-y}MII_yPO_4$ and $Li_3MI_{2-y}MII_y(PO_4)_3$.

In one aspect, MI and MII are the same. In a preferred aspect, MI and MII are different from one

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another.   At least one of MI and MII is an element
capable of an oxidation state higher than that initially
present in the lithium-mixed metal phosphate compound.
Correspondingly, at least one of MI and MII has more than
5      one oxidation state in the phosphate compound, and more
than one oxidation state above the ground state $M^0$. The
term oxidation state and valence state are used in the
art interchangeably.

        In another aspect, both MI and MII may have
10      more than one oxidation state and both may be oxidizable
from the state initially present in the phosphate
compound.  Desirably, MII is a metal or semi-metal having
a +2 oxidation state, and is selected from Groups 2, 12
and 14 of the Periodic Table.  Desirably, MII is selected
15      from non-transition metals and semi-metals.  In one
embodiment, MII has only one oxidation state and is
nonoxidizable from its oxidation state in the lithium-
mixed metal compound.  In another embodiment, MII has
more than one oxidation state.  Examples of semi-metals
20      having more than one oxidation state are selenium and
tellurium; other non-transition metals with more than one
oxidation state are tin and lead.  Preferably, MII is
selected from Mg (magnesium), Ca (calcium), Zn (zinc), Sr
(strontium), Pb (lead), Cd (cadmium), Sn (tin), Ba
25      (barium), and Be (beryllium), and mixtures thereof.  In
another preferred aspect, MII is a metal having a +2
oxidation state and having more than one oxidation state,
and is oxidizable from its oxidation state in lithium-
mixed metal compound.

30      Desirably, MI is selected from Fe (iron), Co
(cobalt), Ni (nickel), Mn (manganese), Cu (copper), V
(vanadium), Sn (tin), Ti (titanium), Cr (chromium), and

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mixtures thereof.  As can be seen, MI is preferably
selected from the first row of transition metals and
further includes tin, and MI preferably initially has a
+2 oxidation state.

5          In a preferred aspect, the product $LiMI_{1-y}MII_yPO_4$
is an olivine structure and the product $Li_3MI_{1-y}(PO_4)_3$ is a
rhombohedral or monoclinic Nasicon structure.  In another
aspect, the term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
10    slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent.  In still another
aspect, any portion of P (phosphorous) may be substituted
by Si (silicon), S (sulfur), and/or As (arsenic); and any
portion of O (oxygen) may be substituted by halogen,
15    preferably F (fluorine).  These aspects are also
disclosed in U.S. Patent Application Serial Numbers
09/105,748 filed June 26, 1998, and 09/274,371 filed
March 23, 1999; and in U.S. Patent No. 5,871,866 issued
February 16, 1999, which is incorporated by reference in
20    its entirety; each of the listed applications and patents
are co-owned by the assignee of the present invention.

          The metal phosphates are alternatively
represented by the nominal general formulas such as
$Li_{1-x}MI_{1-y}MII_yPO_4$ $(0 \leq x \leq 1)$, and $Li_{3-x}MI_{2-y}MII_y(PO_4)_3$
25    signifying capability to release and reinsert lithium.
The term "general" refers to a family of compounds, with
M, x and y representing variations therein.  The
expressions 2-y and 1-y each signify that the relative
amount of MI and MII may vary.  In addition, as stated
30    above, MI may be a mixture of metals meeting the earlier
stated criteria for MI.  In addition, MII may be a
mixture of metallic elements meeting the stated criteria

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for MII.  Preferably, where MII is a mixture, it is a
mixture of 2 metallic elements; and where MI is a
mixture, it is a mixture of 2 metals.  Preferably, each
such metal and metallic element has a +2 oxidation state

5    in the initial phosphate compound.


     The active material of the counter electrode is
any material compatible with the lithium-mixed metal
phosphate of the invention.  Where the lithium-mixed
metal phosphate is used as a positive electrode active

10   material, metallic lithium, lithium-containing material,
or non-lithium-containing material may be used as the
negative electrode active material.  The negative
electrode is desirably a nonmetallic insertion material.
Desirably, the negative electrode comprises an active

15   material from the group consisting of metal oxide,
particularly transition metal oxide, metal chalcogenide,
carbon, graphite, and mixtures thereof.  It is preferred
that the anode active material comprises a carbonaceous
material such as graphite.  The lithium-mixed metal

20   phosphate of the invention may also be used as a negative
electrode material.


     In another embodiment, the present invention
provides a method of preparing a compound of the nominal
general formula $Li_aMI_bMII_c(PO_4)_d$ where $0 < a \leq 3$; the sum

25   of b plus c is greater than zero and up to about 2; and
$0 < d \leq 3$.  Preferred compounds include $Li_3MI_bMII_c(PO_4)_3$
where b plus c is about 2; and $LiMI_bMII_cPO_4$ where b plus c
is about 1.  The method comprises providing starting
materials in particle form.  The starting (precursor)

30   materials include a lithium-containing compound, one or
more metal containing compounds, a compound capable of
providing the phosphate $(PO_4)^{-3}$ anion, and carbon.

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Preferably, the lithium-containing compound is in
particle form, and an example is lithium salt.
Preferably, the phosphate-containing anion compound is in
particle form, and examples include metal phosphate salt
5       and diammonium hydrogen phosphate (DAHP) and ammonium
        dihydrogen phosphate (ADHP). The lithium compound, one
or more metal compounds, and phosphate compound are
included in a proportion which provides the stated
nominal general formula. The starting materials are
10      mixed together with carbon, which is included in an
amount sufficient to reduce the metal ion of one or more
of the metal-containing starting materials without full
reduction to an elemental metal state. Excess quantities
of carbon and one or more other starting materials (i.e.,
15      5 to 10% excess) may be used to enhance product quality.
A small amount of carbon, remaining after the reaction,
functions as a conductive constituent in the ultimate
electrode formulation. This is an advantage since such
remaining carbon is very intimately mixed with the
20      product active material. Accordingly, large quantities of
excess carbon, on the order of 100% excess carbon are
useable in the process. The carbon present during
compound formation is thought to be intimately dispersed
throughout the precursor and product. This provides many
25      advantages, including the enhanced conductivity of the
product. The presence of carbon particles in the
starting materials is also thought to provide nucleation
sites for the production of the product crystals.

        The starting materials are intimately mixed and
30      then reacted together where the reaction is initiated by
heat and is preferably conducted in a nonoxidizing, inert
atmosphere, whereby the lithium, metal from the metal
compound(s), and phosphate combine to form the

$Li_aMI_bMII_c(PO_4)_d$ product. Before reacting the compounds,
the particles are intermingled to form an essentially
homogeneous powder mixture of the precursors. In one
aspect, the precursor powders are dry-mixed using a ball

5    mill, such as zirconia media. Then the mixed powders are
pressed into pellets. In another aspect, the precursor
powders are mixed with a binder. The binder is selected
so as to not inhibit reaction between particles of the
powders. Therefore, preferred binders decompose or

10   evaporate at a temperature less than the reaction
temperature. Examples include mineral oils (i.e.,
glycerol, or C-18 hydrocarbon mineral oil) and polymers
which decompose (carbonize) to form a carbon residue
before the reaction starts, or which evaporate before the

15   reaction starts. In still another aspect, intermingling
is conducted by forming a wet mixture using a volatile
solvent and then the intermingled particles are pressed
together in pellet form to provide good grain-to-grain
contact.

20         Although it is desired that the precursor
compounds be present in a proportion which provides the
stated general formula of the product, the lithium
compound may be present in an excess amount on the order
of 5 percent excess lithium compared to a stoichiometric

25   mixture of the precursors. And the carbon may be present
at up to 100% excess compared to the stoichiometric
amount. The method of the invention may also be used to
prepare other novel products, and to prepare known
products. A number of lithium compounds are available as

30   precursors, such as lithium acetate ($LiOOCCH_3$), lithium
hydroxide, lithium nitrate ($LiNO_3$), lithium oxalate
($Li_2C_2O_4$), lithium oxide ($Li_2O$), lithium phosphate
($Li_3PO_4$), lithium dihydrogen phosphate ($LiH_2PO_4$), lithium

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vanadate (LiVO₃), and lithium carbonate (Li₂CO₃). The
lithium carbonate is preferred for the solid state
reaction since it has a very high melting point and
commonly reacts with the other precursors before melting.

5      Lithium carbonate has a melting point over 600°C and it
decomposes in the presence of the other precursors and/or
effectively reacts with the other precursors before
melting. In contrast, lithium hydroxide melts at about
400°C. At some reaction temperatures preferred herein of

10     over 450°C the lithium hydroxide will melt before any
significant reaction with the other precursors occurs to
an effective extent. This melting renders the reaction
very difficult to control. In addition, anhydrous LiOH
is highly hygroscopic and a significant quantity of water

15     is released during the reaction. Such water needs to be
removed from the oven and the resultant product may need
to be dried. In one preferred aspect, the solid state
reaction made possible by the present invention is much
preferred since it is conducted at temperatures at which

20     the lithium-containing compound reacts with the other
reactants before melting. Therefore, lithium hydroxide
is useable as a precursor in the method of the invention
in combination with some precursors, particularly the
phosphates. The method of the invention is able to be

25     conducted as an economical carbothermal-based process
with a wide variety of precursors and over a relatively
broad temperature range.


The aforesaid precursor compounds (starting
materials) are generally crystals, granules, and powders

30     and are generally referred to as being in particle form.
Although many types of phosphate salts are known, it is
preferred to use diammonium hydrogen phosphate (NH₄)₂HPO₄
(DAHP) or ammonium dihydrogen phosphate (NH₄)H₂PO₄ (ADHP).

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Both ADHP and DAHP meet the preferred criteria that the
precursors decompose in the presence of one another or
react with one another before melting of such precursor.
Exemplary metal compounds are $Fe_2O_3$, $Fe_3O_4$, $V_2O_5$, $VO_2$,
5    $LiVO_3$, $NH_4VO_3$, $Mg(OH)_2$, CaO, MgO, $Ca(OH)_2$, $MnO_2$, $Mn_2O_3$,
$Mn_3(PO_4)_2$, CuO, SnO, $SnO_2$, $TiO_2$, $Ti_2O_3$, $Cr_2O_3$, $PbO_2$, PbO,
$Ba(OH)_2$, BaO, $Cd(OH)_2$. In addition, some starting
materials serve as both the source of metal ion and
phosphate, such as $FePO_4$, $Fe_3(PO_4)_2$, $Zn_3(PO_4)_2$, and
10   $Mg_3(PO_4)_2$. Still others contain both lithium ion and
phosphate such as $Li_3PO_4$ and $LiH_2PO_4$. Other exemplary
precursors are $H_3PO_4$ (phosphoric acid); and $P_2O_5$ ($P_4O_{10}$)
phosphoric oxide; and $HPO_3$ meta phosphoric acid, which is
a decomposition product of $P_2O_5$. If it is desired to
15   replace any of the oxygen with a halogen, such as
fluorine, the starting materials further include a
fluorine compound such as LiF. If it is desired to
replace any of the phosphorous with silicon, then the
starting materials further include silicon oxide ($SiO_2$).
20   Similarly, ammonium sulfate in the starting materials is
useable to replace phosphorus with sulfur.

The starting materials are available from a
number of sources. The following are typical. Vanadium
pentoxide of the formula $V_2O_5$ is obtainable from any
25   number of suppliers including Kerr McGee, Johnson
Matthey, or Alpha Products of Davers, Massachusetts.
Vanadium pentoxide has a CAS number of 1314-62-1. Iron
oxide $Fe_3O_3$ is a common and very inexpensive material
available in powder form from the same suppliers. The
30   other precursor materials mentioned above are also
available from well known suppliers, such as those listed
above.

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The method of the invention may also be used to
react starting materials in the presence of carbon to
form a variety of other novel products, such as gamma-
$LiV_2O_5$ and also to produce known products. Here, the
5   carbon functions to reduce metal ion of a starting metal
compound to provide a product containing such reduced
metal ion. The method is particularly useful to also add
lithium to the resultant product, which thus contains the
metallic element ions, namely, the lithium ion and the
10  other metal ion, thereby forming a mixed metal product.
An example is the reaction of vanadium pentoxide ($V_2O_5$)
with lithium carbonate in the presence of carbon to form
gamma-$LiV_2O_5$. Here the starting metal ion $V^{+5}V^{+5}$ is
reduced to $V^{+4}V^{+5}$ in the final product. A single phase
15  gamma-$LiV_2O_5$ product is not known to have been directly
and independently formed before.

As described earlier, it is desirable to
conduct the reaction at a temperature where the lithium
compound reacts before melting. The temperature should
20  be about 400°C or greater, and desirably 450°C or
greater, and preferably 500°C or greater, and generally
will proceed at a faster rate at higher temperatures.
The various reactions involve production of CO or $CO_2$ as
an effluent gas. The equilibrium at higher temperature
25  favors CO formation. Some of the reactions are more
desirably conducted at temperatures greater than 600°C;
most desirably greater than 650°C; preferably 700°C or
greater; more preferably 750°C or greater. Suitable
ranges for many reactions are about 700 to 950°C, or
30  about 700 to 800°C.

Generally, the higher temperature reactions
produce CO effluent and the stoichiometry requires more

carbon be used than the case where $CO_2$ effluent is produced at lower temperature. This is because the reducing effect of the C to $CO_2$ reaction is greater than the C to CO reaction. The C to $CO_2$ reaction involves an

5    increase in carbon oxidation state of +4 (from 0 to 4) and the C to CO reaction involves an increase in carbon oxidation state of +2 (from ground state zero to 2). Here, higher temperature generally refers to a range of about 650°C to about 1000°C and lower temperature refers

10   to up to about 650°C. Temperatures higher than 1200°C are not thought to be needed.

          In one aspect, the method of the invention utilizes the reducing capabilities of carbon in a unique and controlled manner to produce desired products having

15   structure and lithium content suitable for electrode active materials. The method of the invention makes it possible to produce products containing lithium, metal and oxygen in an economical and convenient process. The ability to lithiate precursors, and change the oxidation

20   state of a metal without causing abstraction of oxygen from a precursor is heretofore unexpected. These advantages are at least in part achieved by the reductant, carbon, having an oxide whose free energy of formation becomes more negative as temperature increases.

25   Such oxide of carbon is more stable at high temperature than at low temperature. This feature is used to produce products having one or more metal ions in a reduced oxidation state relative to the precursor metal ion oxidation state. The method utilizes an effective

30   combination of quantity of carbon, time and temperature to produce new products and to produce known products in a new way.

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Referring back to the discussion of
temperature, at about 700°C both the carbon to carbon
monoxide and the carbon to carbon dioxide reactions are
occurring. At closer to 600°C the C to $CO_2$ reaction is

5      the dominant reaction. At closer to 800°C the C to CO
reaction is dominant. Since the reducing effect of the C
to $CO_2$ reaction is greater, the result is that less
carbon is needed per atomic unit of metal to be reduced.
In the case of carbon to carbon monoxide, each atomic

10     unit of carbon is oxidized from ground state zero to plus
2. Thus, for each atomic unit of metal ion (M) which is
being reduced by one oxidation state, one half atomic
unit of carbon is required. In the case of the carbon to
carbon dioxide reaction, one quarter atomic unit of

15     carbon is stoichiometrically required for each atomic
unit of metal ion (M) which is reduced by one oxidation
state, because carbon goes from ground state zero to a
plus 4 oxidation state. These same relationships apply
for each such metal ion being reduced and for each unit

20     reduction in oxidation state desired.

It is preferred to heat the starting materials
at a ramp rate of a fraction of a degree to 10°C per
minute and preferably about 2°C per minute. Once the
desired reaction temperature is attained, the reactants

25     (starting materials) are held at the reaction temperature
for several hours. The heating is preferably conducted
under non-oxidizing or inert gas such as argon or vacuum.
Advantageously, a reducing atmosphere is not required,
although it may be used if desired. After reaction, the

30     products are preferably cooled from the elevated
temperature to ambient (room) temperature (i.e., 10°C to
40°C). Desirably, the cooling occurs at a rate similar
to the earlier ramp rate, and preferably 2°C/minute

cooling.  Such cooling rate has been found to be adequate
to achieve the desired structure of the final product.
It is also possible to quench the products at a cooling
rate on the order of about 100°C/minute.  In some
5    instances, such rapid cooling (quench) may be preferred.

        The present invention resolves the capacity
problem posed by widely used cathode active material. It
has been found that the capacity and capacity retention
of cells having the preferred active material of the
10   invention are improved over conventional materials.
Optimized cells containing lithium-mixed metal phosphates
of the invention potentially have performance improved
over commonly used lithium metal oxide compounds.
Advantageously, the new method of making the novel
15   lithium-mixed metal phosphate compounds of the invention
is relatively economical and readily adaptable to
commercial production.

        Objects, features, and advantages of the
invention include an electrochemical cell or battery
20   based on lithium-mixed metal phosphates.  Another object
is to provide an electrode active material which combines
the advantages of good discharge capacity and capacity
retention.  It is also an object of the present invention
to provide electrodes which can be manufactured
25   economically.  Another object is to provide a method for
forming electrode active material which lends itself to
commercial scale production for preparation of large
quantities.

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These and other objects, features, and
advantages will become apparent from the following
description of the preferred embodiments, claims, and
accompanying drawings.

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## Brief Description of the Drawings

**Figure 1** shows the results of an x-ray
diffraction analysis, of the $LiFePO_4$ prepared according
to the invention using CuKα radiation, λ = 1.5405Å.  Bars
5     refer to simulated pattern from refined cell parameters,
Space Group, SG = Pnma (62).  The values are a = 10.2883Å
(0.0020), b = 5.9759Å (0.0037), c = 4.6717Å (0.0012)
0.0072, cell volume = 287.2264Å$^3$ (0.0685).  Density, p =
3.605 g/cc, zero = 0.452 (0.003).  Peak at full width
10    half maximum, PFWHM = 0.21.  Crystallite size from XRD
data = 704Å.

**Figure 2** is a voltage/capacity plot of $LiFePO_4$-
containing cathode cycled with a lithium metal anode
using constant current cycling at ± 0.2 milliamps per
15    square centimeter in a range of 2.5 to 4.0 volts at a
temperature of about 23°C.  The cathode contained 19.0mg
of the $LiFePO_4$ active material, prepared by the method of
the invention.  The electrolyte comprised ethylene
carbonate (EC) and dimethyl carbonate (DMC) in a weight
20    ratio of 2:1 and included a 1 molar concentration of
$LiPF_6$ salt.  The lithium-metal-phosphate containing
electrode and the lithium metal counter electrode are
maintained spaced apart by a glass fiber separator which
is interpenetrated by the solvent and the salt.

25    **Figure 3** shows multiple constant current
cycling of $LiFePO_4$ active material cycled with a lithium
metal anode using the electrolyte as described in
connection with **Figure 2** and cycled, charge and discharge
at ± 0.2 milliamps per square centimeter, 2.5 to 4.0
30    volts at two different temperature conditions, 23°C and
60°C.  **Figure 3** shows the excellent rechargeability of

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the lithium iron phosphate/lithium metal cell, and also shows the excellent cycling and specific capacity (mAh/g) of the active material.

Figure 4 shows the results of an x-ray
5   diffraction analysis, of the $LiFe_{0.9}Mg_{0.1}PO_4$ prepared according to the invention, using $CuK\alpha$ radiation, $\lambda$ = 1.5405Å. Bars refer to simulated pattern from refined cell parameters SG = Pnma (62). The values are a = 10.2688Å (0.0069), b = 5.9709Å (0.0072), c = 4.6762Å
10   (0.0054), cell volume = 286.7208Å (0.04294), p = 3.617 g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite = 950Å.

Figure 5 is a voltage/capacity plot of
$LiFe_{0.9}Mg_{0.1}PO_4$-containing cathode cycled with a lithium
15   metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts. Other conditions are as described earlier with respect to Figure 2. The cathode contained 18.9mg of the $LiFe_{0.9}Mg_{0.1}PO_4$ active material prepared by the method of
20   the invention.

Figure 6 shows multiple constant current cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with a lithium metal anode using the electrolyte as described in connection with Figure 2 and cycled, charge and discharge at ± 0.2
25   milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions, 23°C and 60°C. Figure 6 shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

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Figure 7 is a voltage/capacity plot of
$LiFe_{0.8}Mg_{0.2}PO_4$-containing cathode cycled with a lithium
metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
5      volts at 23°C.  Other conditions are as described earlier
with respect to Figure 2.  The cathode contained 16mg of
the $LiFe_{0.8}Mg_{0.2}PO_4$ active material prepared by the method
of the invention.

Figure 8 shows the results of an x-ray
10     diffraction analysis, of the $LiFe_{0.9}Ca_{0.1}PO_4$ prepared
according to the invention, using CuKα radiation, λ =
1.5405Å.  Bars refer to simulated pattern from refined
cell parameters SG = Pnma (62).  The values are a =
10.3240Å (0.0045), b = 6.0042Å (0.0031), c = 4.6887Å
15     (0.0020), cell volume = 290.6370Å (0.1807), zero = 0.702
(0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite =
680Å.

Figure 9 is a voltage/capacity plot of
$LiFe_{0.8}Ca_{0.2}PO_4$-containing cathode cycled with a lithium
20     metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
volts at 23°.  Other conditions are as described earlier
with respect to Figure 2.  The cathode contained 18.5mg
of the $LiFe_{0.8}Ca_{0.2}PO_4$ active material prepared by the
25     method of the invention.

Figure 10 is a voltage/capacity plot of
$LiFe_{0.8}Zn_{0.2}PO_4$-containing cathode cycled with a lithium
metal anode using constant current cycling at ± 0.2
milliamps per square centimeter in a range of 2.5 to 4.0
30     volts at 23°C.  Other conditions are as described earlier
with respect to Figure 2.  The cathode contained 18.9mg

of the $LiFe_{0.8}Zn_{0.2}PO_4$ active material prepared by the
method of the invention.

Figure 11 shows the results of an x-ray
diffraction analysis of the gamma-$Li_xV_2O_5$ (x = 1, gamma
5      $LiV_2O_5$) prepared according to the invention using CuKα
radiation λ = 1.5405Å.   The values are a = 9.687Å (1), b
= 3.603Å (2), and c = 10.677Å (3); phase type is gamma-
$Li_xV_2O_5$ (x = 1); symmetry is orthorhombic; and space group
is Pnma.

10          Figure 12 is a voltage/capacity plot of gamma-
$LiV_2O_5$-containing cathode cycled with a lithium metal
anode using constant current cycling at ± 0.2 milliamps
per square centimeter in a range of 2.5 to 3.8 volts at
23°C.   Other conditions are as described earlier with
15     respect to Figure 2.   The cathode contained 21mg of the
gamma-$LiV_2O_5$ active material prepared by the method of
the invention.

Figure 13 is a two-part graph based on multiple
constant current cycling of gamma-$LiV_2O_5$ cycled with a
20     lithium metal anode using the electrolyte as described in
connection with Figure 2 and cycled, charge and discharge
at ± 0.2 milliamps per square centimeter, 2.5 to 3.8
volts.   In the two-part graph, Figure 13 shows the
excellent rechargeability of the lithium-metal-
25     oxide/lithium metal cell.   Figure 13 shows the excellent
cycling and capacity of the cell.

Figure 14 shows the results of an x-ray
diffraction analysis of the $Li_3V_2(PO_4)_3$ prepared according
to the invention.   The analysis is based on CuKα

radiation, $\lambda$ = 1.5405Å.  The values are a = 12.184Å (2),
b = 8.679Å (2), c = 8.627Å (3), and $\beta$ = 90.457° (4).


**Figure 15** shows the results of an x-ray
diffraction analysis of $Li_3V_2(PO_4)_3$ prepared according to

5    a method described in U.S. Patent No. 5,871,866.  The
analysis is based on CuK$\alpha$ radiation, $\lambda$ = 1.5405Å.  The
values are a = 12.155Å (2), b = 8.711Å (2), c = 8.645Å
(3); the angle beta is 90.175 (6); symmetry is
Monoclinic; and space group is $P2_1/n$.


10          **Figure 16** is an EVS (Electrochemical Voltage
Spectroscopy) voltage/capacity profile for a cell with
cathode material formed by the carbothermal reduction
method of the invention.  The cathode material is 13.8mg
of $Li_3V_2(PO_4)_3$. The cell includes a lithium metal counter

15   electrode in an electrolyte comprising ethylene carbonate
(EC) and dimethyl carbonate (DMC) in a weight ratio of
2:1 and including a 1 molar concentration of $LiPF_6$ salt.
The lithium-metal-phosphate containing electrode and the
lithium metal counter electrode are maintained spaced

20   apart by a fiberglass separator which is interpenetrated
by the solvent and the salt.  The conditions are ± 10 mV
steps, between about 3.0 and 4.2 volts, and the critical
limiting current density is less than or equal to 0.1
$mA/cm^2$.


25          **Figure 17** is an EVS differential capacity
versus voltage plot for the cell as described in
connection with **Figure 16**.


          **Figure 18** shows multiple constant current
cycling of $LiFe_{0.8}Mg_{0.2}PO_4$ cycled with a lithium metal

30   anode using the electrolyte as described in connection

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with **Figure 2** and cycled, charge and discharge at ± 0.2
milliamps per square centimeter, 2.5 to 4.0 volts at two
different temperature conditions, 23°C and 60°C. **Figure
18** shows the excellent rechargeability of the lithium-

5      metal-phosphate/lithium metal cell, and also shows the
excellent cycling and capacity of the cell.

       **Figure 19** is a graph of potential over time for
the first four complete cycles of the $LiMg_{0.1}Fe_{0.9}PO_4$/MCMB
graphite cell of the invention.

10     **Figure 20** is a two-part graph based on multiple
constant current cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with an
MCMB graphite anode using the electrolyte as described in
connection with **Figure 2** and cycled, charge and discharge
at ± 0.2 milliamps per square centimeter, 2.5 to 3.6

15     volts, 23°C and based on a C/10 (10 hour) rate. In the
two-part graph, **Figure 20** shows the excellent
rechargeability of the lithium-metal-phosphate/graphite
cell. **Figure 20** shows the excellent cycling and capacity
of the cell.

20     **Figure 21** is a graph of potential over time for
the first three complete cycles of the gamma-$LiV_2O_5$/MCMB
graphite cell of the invention.

       **Figure 22** is a diagrammatic representation of a
typical laminated lithium-ion battery cell structure.

25     **Figure 23** is a diagrammatic representation of a
typical multi-cell battery cell structure.

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## Detailed Description of the Preferred Embodiments

The present invention provides lithium-mixed
metal-phosphates, which are usable as electrode active
materials, for lithium ($Li^+$) ion removal and insertion.

5    Upon extraction of the lithium ions from the lithium-
mixed-metal-phosphates, significant capacity is achieved.
In one aspect of the invention, electrochemical energy is
provided when combined with a suitable counter electrode
by extraction of a quantity x of lithium from lithium-

10   mixed-metal-phosphates $Li_{a-x}MI_bMII_c(PO_4)_d$. When a quantity
x of lithium is removed per formula unit of the lithium-
mixed-metal phosphate, metal MI is oxidized. In another
aspect, metal MII is also oxidized. Therefore, at least
one of MI and MII is oxidizable from its initial

15   condition in the phosphate compound as Li is removed.
Consider the following which illustrate the mixed metal
compounds of the invention: $LiFe_{1-y}Sn_yPO_4$, has two
oxidizable elements, Fe and Sn; in contrast,
$LiFe_{1-y}Mg_yPO_4$ has one oxidizable metal, the metal Fe.

20   In another aspect, the invention provides a
lithium ion battery which comprises an electrolyte; a
negative electrode having an insertion active material;
and a positive electrode comprising a lithium-mixed-
metal-phosphate active material characterized by an

25   ability to release lithium ions for insertion into the
negative electrode active material. The lithium-mixed-
metal-phosphate is desirably represented by the nominal
general formula $Li_aMI_bMII_c(PO_4)_d$. Although the metals MI
and MII may be the same, it is preferred that the metals

30   MI and MII are different. Desirably, in the phosphate
compound MI is a metal selected from the group: Fe, Co,
Ni, Mn, Cu, V, Sn, Ti, Cr and mixtures thereof, and MI is

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most desirably a transition metal or mixture thereof
selected from said group. Most preferably, MI has a +2
valence or oxidation state.

   In another aspect, MII is selected from Mg, Ca,
5   Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Most
preferably, MII has a +2 valence or oxidation state. The
lithium-mixed-metal-phosphate is preferably a compound
represented by the nominal general formula
$Li_{a-x}MI_bMII_c(PO_4)_d$, signifying the preferred composition
10   and its capability to release x lithium. Accordingly,
during cycling, charge and discharge, the value of x
varies as x greater than or equal to 0 and less than or
equal to a. The present invention resolves a capacity
problem posed by conventional cathode active materials.
15   Such problems with conventional active materials are
described by Tarascon in U.S. Patent No. 5,425,932, using
$LiMn_2O_4$ as an example. Similar problems are observed
with $LiCoO_2$, $LiNiO_2$, and many, if not all, lithium metal
chalcogenide materials. The present invention
20   demonstrates that significant capacity of the cathode
active material is utilizable and maintained.

   A preferred novel procedure for forming the
lithium-mixed-metal-phosphate $Li_aMI_bMII_c(PO_4)_d$ compound
active material will now be described. In addition, the
25   preferred novel procedure is also applicable to formation
of other lithium metal compounds, and will be described
as such. The basic procedure will be described with
reference to exemplary starting materials but is not
limited thereby. The basic process comprises conducting
30   a reaction between a lithium compound, preferably lithium
carbonate ($Li_2CO_3$), metal compound(s), for example,
vanadium pentoxide ($V_2O_5$), iron oxide ($Fe_2O_3$), and/or

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manganese hydroxide, and a phosphoric acid derivative,
preferably the phosphoric acid ammonium salt, diammonium
hydrogen phosphate, $(NH_4)_2H(PO_4)$. Each of the precursor
starting materials are available from a number of
5    chemical outfits including Aldrich Chemical Company and
Fluka. Using the method described herein, $LiFePO_4$ and
$LiFe_{0.9}Mg_{0.1}PO_4$, $Li_3V_2(PO_4)_3$ were prepared with approximately
a stoichiometric amount of $Li_2CO_3$, the respective metal
compound, and $(NH_4)_2HPO_4$. Carbon powder was included with
10    these precursor materials. The precursor materials were
initially intimately mixed and dry ground for about 30
minutes. The intimately mixed compounds were then
pressed into pellets. Reaction was conducted by heating
in an oven at a preferred ramped heating rate to an
15    elevated temperature, and held at such elevated
temperature for several hours to complete formation of
the reaction product. The entire reaction was conducted
in a non-oxidizing atmosphere, under flowing pure argon
gas. The flow rate will depend upon the size of the oven
20    and the quantity needed to maintain the atmosphere. The
oven was permitted to cool down at the end of the
reaction period, where cooling occurred at a desired rate
under argon. Exemplary and preferred ramp rates,
elevated reaction temperatures and reaction times are
25    described herein. In one aspect, a ramp rate of
$2°$/minute to an elevated temperature in a range of 750°C
to 800°C was suitable along with a dwell (reaction time)
of 8 hours. Refer to Reactions 1, 2, 3 and 4 herein. In
another variation per Reaction 5, a reaction temperature
30    of 600°C was used along with a dwell time of about one
hour. In still another variation, as per Reaction 6, a
two-stage heating was conducted, first to a temperature
of 300°C and then to a temperature of 850°.

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The general aspects of the above synthesis
route are applicable to a variety of starting materials.
Lithium-containing compounds include $Li_2O$ (lithium
oxide), $LiH_2PO_4$ (lithium hydrogen phosphate),
5      $Li_2C_2O_4$ (lithium oxalate), LiOH (lithium hydroxide),
$LiOH.H_2O$ (lithium hydroxide monohydride), and $LiHCO_3$
(lithium hydrogen carbonate). The metal compounds(s) are
reduced in the presence of the reducing agent, carbon.
The same considerations apply to other lithium-metal- and
10     phosphate-containing precursors. The thermodynamic
considerations such as ease of reduction, of the selected
precursors, the reaction kinetics, and the melting point
of the salts will cause adjustment in the general
procedure, such as, amount of carbon reducing agent, and
15     the temperature of reaction.

Figures 1 through 21 which will be described
more particularly below show characterization data and
capacity in actual use for the cathode materials
(positive electrodes) of the invention. Some tests were
20     conducted in a cell comprising a lithium metal counter
electrode (negative electrode) and other tests were
conducted in cells having a carbonaceous counter
electrode. All of the cells had an $EC:DMC-LiPF_6$
electrolyte.

25     Typical cell configurations will now be
described with reference to Figures 22 and 23; and such
battery or cell utilizes the novel active material of the
invention. Note that the preferred cell arrangement
described here is illustrative and the invention is not
30     limited thereby. Experiments are often performed, based
on full and half cell arrangements, as per the following
description. For test purposes, test cells are often

fabricated using lithium metal electrodes. When forming
cells for use as batteries, it is preferred to use an
insertion positive electrode as per the invention and a
graphitic carbon negative electrode.

5          A typical laminated battery cell structure 10
is depicted in **Figure 22**. It comprises a negative
electrode side 12, a positive electrode side 14, and an
electrolyte/separator 16 there between. Negative
electrode side 12 includes current collector 18, and
10    positive electrode side 14 includes current collector 22.
A copper collector foil 18, preferably in the form of an
open mesh grid, upon which is laid a negative electrode
membrane 20 comprising an insertion material such as
carbon or graphite or low-voltage lithium insertion
15    compound, dispersed in a polymeric binder matrix. An
electrolyte/separator film 16 membrane is preferably a
plasticized copolymer. This electrolyte/separator
preferably comprises a polymeric separator and a suitable
electrolyte for ion transport. The electrolyte/separator
20    is positioned upon the electrode element and is covered
with a positive electrode membrane 24 comprising a
composition of a finely divided lithium insertion
compound in a polymeric binder matrix. An aluminum
collector foil or grid 22 completes the assembly.
25    Protective bagging material 40 covers the cell and
prevents infiltration of air and moisture.

          In another embodiment, a multi-cell battery
configuration as per **Figure 23** is prepared with copper
current collector 51, negative electrode 53,
30    electrolyte/separator 55, positive electrode 57, and
aluminum current collector 59. Tabs 52 and 58 of the
current collector elements form respective terminals for

the battery structure.  As used herein, the terms "cell"
and "battery" refer to an individual cell comprising
anode/electrolyte/cathode and also refer to a multi-cell
arrangement in a stack.

5          The relative weight proportions of the
components of the positive electrode are generally:  50-
90% by weight active material; 5-30% carbon black as the
electric conductive diluent; and 3-20% binder chosen to
hold all particulate materials in contact with one
10     another without degrading ionic conductivity.  Stated
ranges are not critical, and the amount of active
material in an electrode may range from 25-95 weight
percent.  The negative electrode comprises about 50-95%
by weight of a preferred graphite, with the balance
15     constituted by the binder.  A typical electrolyte
separator film comprises approximately two parts polymer
for every one part of a preferred fumed silica.  The
conductive solvent comprises any number of suitable
solvents and salts.  Desirable solvents and salts are
20     described in U.S. Patent Nos. 5,643,695 and 5,418,091.
One example is a mixture of EC:DMC:LiPF$_6$ in a weight
ratio of about 60:30:10.

           Solvents are selected to be used individually
or in mixtures, and include dimethyl carbonate (DMC),
25     diethylcarbonate (DEC), dipropylcarbonate (DPC),
ethylmethylcarbonate (EMC), ethylene carbonate (EC),
propylene carbonate (PC), butylene carbonate, lactones,
esters, glymes, sulfoxides, sulfolanes, etc.  The
preferred solvents are EC/DMC, EC/DEC, EC/DPC and EC/EMC.
30     The salt content ranges from 5% to 65% by weight,
preferably from 8% to 35% by weight.

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Those skilled in the art will understand that
any number of methods are used to form films from the
casting solution using conventional meter bar or doctor
blade apparatus.  It is usually sufficient to air-dry the
5   films at moderate temperature to yield self-supporting
films of copolymer composition.  Lamination of assembled
cell structures is accomplished by conventional means by
pressing between metal plates at a temperature of about
120-160°C.  Subsequent to lamination, the battery cell
10   material may be stored either with the retained
plasticizer or as a dry sheet after extraction of the
plasticizer with a selective low-boiling point solvent.
The plasticizer extraction solvent is not critical, and
methanol or ether are often used.

15   Separator membrane element 16 is generally
polymeric and prepared from a composition comprising a
copolymer.  A preferred composition is the 75 to 92%
vinylidene fluoride with 8 to 25% hexafluoropropylene
copolymer (available commercially from Atochem North
20   America as Kynar FLEX) and an organic solvent
plasticizer.  Such a copolymer composition is also
preferred for the preparation of the electrode membrane
elements, since subsequent laminate interface
compatibility is ensured.  The plasticizing solvent may
25   be one of the various organic compounds commonly used as
solvents for electrolyte salts, e.g., propylene carbonate
or ethylene carbonate, as well as mixtures of these
compounds.  Higher-boiling plasticizer compounds such as
dibutyl phthalate, dimethyl phthalate, diethyl phthalate,
30   and tris butoxyethyl phosphate are particularly suitable.
Inorganic filler adjuncts, such as fumed alumina or
silanized fumed silica, may be used to enhance the
physical strength and melt viscosity of a separator

membrane and, in some compositions, to increase the
subsequent level of electrolyte solution absorption.

In the construction of a lithium-ion battery, a
current collector layer of aluminum foil or grid is
5    overlaid with a positive electrode film, or membrane,
separately prepared as a coated layer of a dispersion of
insertion electrode composition. This is typically an
insertion compound such as $LiMn_2O_4$ (LMO), $LiCoO_2$, or
$LiNiO_2$, powder in a copolymer matrix solution, which is
10   dried to form the positive electrode. An
electrolyte/separator membrane is formed as a dried
coating of a composition comprising a solution containing
VdF:HFP copolymer and a plasticizer solvent is then
overlaid on the positive electrode film. A negative
15   electrode membrane formed as a dried coating of a
powdered carbon or other negative electrode material
dispersion in a VdF:HFP copolymer matrix solution is
similarly overlaid on the separator membrane layer. A
copper current collector foil or grid is laid upon the
20   negative electrode layer to complete the cell assembly.
Therefore, the VdF:HFP copolymer composition is used as a
binder in all of the major cell components, positive
electrode film, negative electrode film, and
electrolyte/separator membrane. The assembled components
25   are then heated under pressure to achieve heat-fusion
bonding between the plasticized copolymer matrix
electrode and electrolyte components, and to the
collector grids, to thereby form an effective laminate of
cell elements. This produces an essentially unitary and
30   flexible battery cell structure.

Examples of forming cells containing metallic
lithium anode, insertion electrodes, solid electrolytes

and liquid electrolytes can be found in U.S. Patent Nos.
4,668,595; 4,830,939; 4,935,317; 4,990,413; 4,792,504;
5,037,712; 5,262,253; 5,300,373; 5,435,054; 5,463,179;
5,399,447; 5,482,795 and 5,411,820; each of which is
5    incorporated herein by reference in its entirety.  Note
that the older generation of cells contained organic
polymeric and inorganic electrolyte matrix materials,
with the polymeric being most preferred. . The
polyethylene oxide of 5,411,820 is an example.  More
10   modern examples are the VdF:HFP polymeric matrix.
Examples of casting, lamination and formation of cells
using VdF:HFP are as described in U.S. Patent Nos.
5,418,091; 5,460,904; 5,456,000; and 5,540,741; assigned
to Bell Communications Research, each of which is
15   incorporated herein by reference in its entirety.

. As described earlier, the electrochemical cell
operated as per the invention, may be prepared in a
variety of ways.  In one embodiment, the negative
electrode may be metallic lithium. In more desirable
20   embodiments, the negative electrode is an insertion
active material, such as, metal oxides and graphite.
When a metal oxide active material is used, the
components of the electrode are the metal oxide,
electrically conductive carbon, and binder, in
25   proportions similar to that described above for the
positive electrode. In a preferred embodiment, the
negative electrode active material is graphite particles.
For test purposes, test cells are often fabricated using
lithium metal electrodes.  When forming cells for use as
30   batteries, it is preferred to use an insertion metal
oxide positive electrode and a graphitic carbon negative
electrode.  Various methods for fabricating
electrochemical cells and batteries and for forming

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electrode components are described herein.  The invention
is not, however, limited by any particular fabrication
method.

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## Formation of Active Materials

**EXAMPLE I**

Reaction 1(a). LiFePO$_4$ formed from FePO$_4$

$$FePO_4 + 0.5 \ Li_2CO_3 + 0.5 \ C \rightarrow LiFePO_4 + 0.5 \ CO_2 + 0.5 \ CO$$
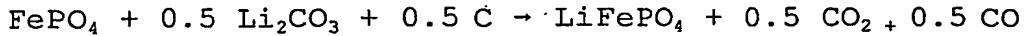
5      (a)   Pre-mix reactants in the following proportions using ball mill. Thus,

|  |  |
|---|---|
| 1 mol FePO$_4$ | 150.82g |
| 0.5 mol Li$_2$CO$_3$ | 36.95g |
| 0.5 mol carbon | 6.0g |

10            (but use <u>100%</u> excess carbon → 12.00g)

        (b)   Pelletize powder mixture

        (c)   Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

15      (d)   Cool to room temperature at 2°/minute under argon.

        (e)   Powderize pellet.

            Note that at 750°C this is predominantly a CO reaction. This reaction is able to be

20            conducted at a temperature in a range of about 700°C to about 950°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum.

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**EXAMPLE II**

Reaction 1(b). $LiFePO_4$ formed from $Fe_2O_3$

$$0.5\ Fe_2O_3 + 0.5\ Li_2CO_3 + (NH_4)_2HPO_4 + 0.5\ C \rightarrow LiFePO_4 +$$
$$0.5\ CO_2 + 2\ NH_3 + 3/2\ H_2O + 0.5\ CO$$
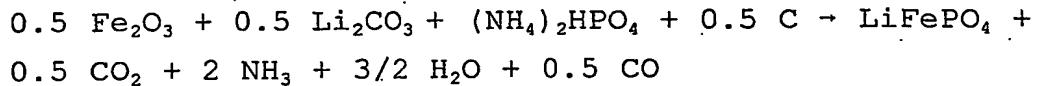
5          (a)   Premix powders in the following proportions

|  |  |
|---|---|
| 0.5 mol $Fe_2O_3$ | 79.85g |
| 0.5 mol $Li_2CO_3$ | 36.95g |
| 1 mol $(NH_4)_2HPO_4$ | 132.06g |
| 0.5 mol carbon | 6.00g |

10          (use 100% excess carbon → 12.00g)

          (b)   Pelletize powder mixture

          (c)   Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

15          (d)   Cool to room temperature at 2°/minute under argon.

          (e)   Powderize

**EXAMPLE III**

Reaction 1(c). $LiFePO_4$ – from $Fe_3(PO_4)_2$

20          Two steps:

Part I.    Carbothermal preparation of $Fe_3(PO_4)_2$


$$3/2\ Fe_2O_3\ +\ 2\,(NH_4)_2HPO_4\ +\ 3/2\ C\ \rightarrow\ Fe_3(PO_4)_2\ +$$

$$3/2\ CO\ +\ 4NH_3\ +\ 5/2\ H_2O$$
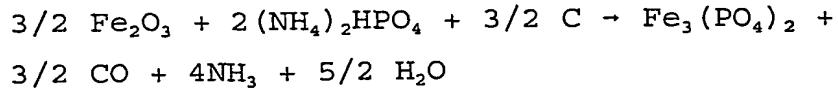
    (a)    Premix reactants in the following proportions

5            3/2 mol $Fe_2O_3$        239.54g

           2 mol $(NH_4)_2HPO_4$    264.12g

           3/2 mol carbon       18.00g


    (use 100% excess carbon → 36.00g)


    (b)    Pelletize powder mixture


10     (c)    Heat pellet to 800°C at a rate of 2°/minute in
          flowing inert atmosphere (e.g. argon).  Dwell
          for 8 hours at 750°C under argon.


    (d)    Cool to room temperature at 2°C/minute under
          argon.


15     (e)    Powderize pellet.


Part II.    Preparation of $LiFePO_4$ from the $Fe_3(PO_4)_2$ of
          Part I.


$$Li_3PO_4\ +\ Fe_3(PO_4)_2\ \rightarrow\ 3\ LiFePO_4$$

    (a)    Premix reactants in the following proportions

20           1 mol $Li_3PO_4$        115.79g

          1 mol $Fe_3(PO_4)_2$     357.48g


    (b)    Pelletize powder mixture

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(c)   Heat pellet to 750°C at a rate of 2°/minute in
      flowing inert atmosphere (e.g. argon).  Dwell
      for 8 hours at 750°C under argon.

(d)   Cool to room temperature at 2°C/minute under

5     argon.

(e)   Powderize pellet.

**EXAMPLE IV**

Reaction 2(a).  $LiFe_{0.9}Mg_{0.1}PO_4$  $(LiFe_{1-y}Mg_yPO_4)$ formed from
$FePO_4$

10        $0.5\ Li_2CO_3 + 0.9\ FePO_4 + 0.1\ Mg(OH)_2 + 0.1(NH_4)_2HPO_4 +$
          $0.45C \rightarrow LiFe_{0.9}Mg_{0.1}PO_4 + 0.5CO_2 + 0.45CO + 0.2NH_3 +$
          $0.25\ H_2O$
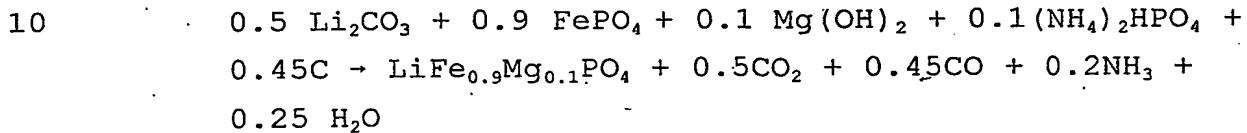
(a)   Pre-mix reactants in the following proportions

|  |  |  |
|---|---|---|
| 0.50 mol $Li_2CO_3$ | = | 36.95g |
| 0.90 mol $FePO_4$ | = | 135.74g |
| 0.10 mol $Mg(OH)_2$ | = | 5.83g |
| 0.10 mol $(NH_4)_2HPO_4$ | = | 1.32g |
| 0.45 mol carbon | = | 5.40g |

(use 100% excess carbon → 10.80g)

20    (b)   Pelletize powder mixture

(c)   Heat to 750°C at a rate of 2°/minute in argon.
      Hold for 8 hours dwell at 750°C in argon

(d)   Cool at a rate of  2°/minute

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(e)    Powderize pellet.


**EXAMPLE V**

Reaction 2(b).  $LiFe_{0.9}Mg_{0.1}PO4$  ($LiFe_{1-y}Mg_yPO_4$) formed from

5    $Fe_2O_3$


0.50 $Li_2CO_3$ + 0.45 $Fe_2O_3$ + 0.10 $Mg(OH)_2$ + $(NH_4)_2HPO_4$ +

0.45C →    $LiFe_{0.9}Mg_{0.1}PO_4$ + 0.5 $CO_2$ + 0.45 CO + 2 $NH_3$ +

1.6 $H_2O$
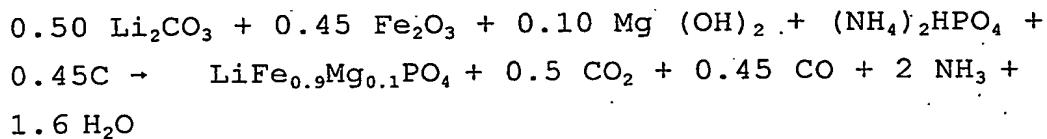

10    (a)    Pre-mix reactants in following ratio

| | | |
|---|---|---|
| 0.50 mol $Li_2CO_3$ | = | 36.95g |
| 0.45 mol $Fe_2O_3$ | = | 71.86g |
| 0.10 mol $Mg(OH)_2$ | = | 5.83g |
| 1.00 mol $(NH_4)_2HPO_4$ | = | 132.06g |
| 0.45 mol carbon | = | 5.40g |

15

(use 100% excess carbon → 10.80g)


(b)    Pelletize powder mixture


(c)    Heat to 750°C at a rate of 2°/minute in argon.
       Hold for 8 hours dwell at 750°C in argon


20    (d)    Cool at a rate of  2°/minute


(e)    Powderize pellet.

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**EXAMPLE VI**

Reaction 2(c). $LiFe_{0.9}Mg_{0.1}PO_4$ ($LiFe_{1-y}Mg_yPO_4$) formed from $LiH_2PO_4$

5      $1.0\ LiH_2PO_4 + 0.45\ Fe_2O_3 + 0.10\ Mg(OH)_2 + 0.45C \rightarrow$
       $LiFe_{0.9}Mg_{0.1}PO_4 + 0.45\ CO + 1.1\ H_2O$
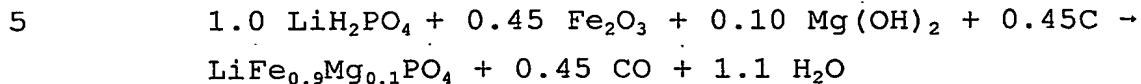
   (a)   Pre-mix reactants in the following proportions

| | | |
|---|---|---|
| 1.00 mol $LiH_2PO_4$ | = | 103.93g |
| 0.45 mol $Fe_2O_3$ | = | 71.86g |
| 0.10 mol $Mg(OH)_2$ | = | 5.83g |
| 0.45 mol carbon | = | 5.40g |

   (use 100% excess carbon → 10.80g)

   (b)   Pelletize powder mixture

15   (c)   Heat to 750°C at a rate of 2°/minute in argon.
             Hold for 8 hours dwell at 750°C in argon

   (d)   Cool at a rate of  2°/minute

   (e)   Powderize pellet.

**EXAMPLE VII**

20   Reaction 3.      Formation of $LiFe_{0.9}Ca_{0.1}PO_4$
       ($LiFe_{1-y}Ca_yPO_4$) from $Fe_2O_3$
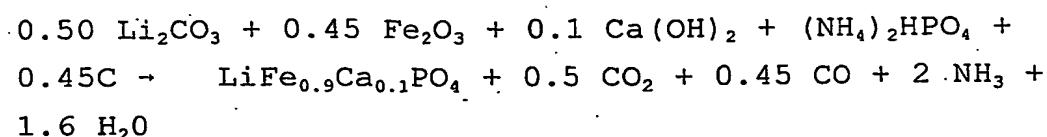
       $0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.1\ Ca(OH)_2 + (NH_4)_2HPO_4 +$
       $0.45C \rightarrow\ LiFe_{0.9}Ca_{0.1}PO_4 + 0.5\ CO_2 + 0.45\ CO + 2\ NH_3 +$
       $1.6\ H_2O$

(a)   Pre-mix reactants in the following proportions

| | | |
|---|---|---|
| 0.50 mol $Li_2CO_3$ | = | 36.95g |
| 0.45 mol $Fe_2O_3$ | = | 71.86g |
| 0.10 mol $Ca(OH)_2$ | = | 7.41g |
| 1.00 mol $(NH_4)_2HPO_4$ | = | 132.06g |
| 0.45 mol carbon | = | 5.40g |

5

(100% excess carbon → 10.80g)

(b)   Pelletize powder mixture

10   (c)   Heat to 750°C at a rate of 2°/minute in argon.
Hold for 8 hours dwell at 750°C in argon

(d)   Cool at a rate of   2°/minute

(e)   Powderize pellet.

**EXAMPLE VIII**

15   Reaction 4.       Formation of $LiFe_{0.9}Zn_{0.1}PO_4$
($LiFe_{1-y}Zn_yPO_4$) from $Fe_2O_3$.

$0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.033\ Zn_3(PO_4)_2 +$
$0.933\ (NH_4)_2HPO_4 + 0.45\ C → LiFe_{0.9}Zn_{0.1}PO_4 + 0.50\ CO_2 +$
$0.45\ CO + 1.866\ NH_3 + 1.2\ H_2O$
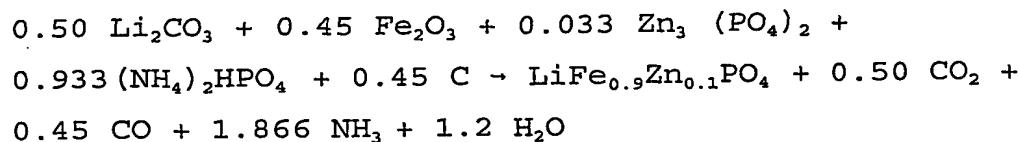
20   Pre-mix reactants in the following proportions

| | | |
|---|---|---|
| 0.50 mol $Li_2CO_3$ | = | 36.95g |
| 0.45 mol $Fe_2O_3$ | = | 71.86g |
| 0.033 mol $Zn_3(PO_4)_2$ | = | 12.74g |
| 0.933 mol $(NH_4)_2HPO_4$ | = | 123.21g |

40

$$0.45 \text{ mol carbon} \quad = \quad 5.40\text{g}$$

(100% excess carbon → 10.80g)

(b)   Pelletize powder mixture

(c)   Heat to 750°C at a rate of 2°/minute in argon.
      Hold for 8 hours dwell at 750°C in argon

(d)   Cool at a rate of 2°/minute

(e)   Powderize pellet.


**EXAMPLE IX**


Reaction 5.   Formation of gamma-$LiV_2O_5$ (γ)

$$V_2O_5 + 0.5 \; Li_2CO_3 + 0.25 \; C \;\rightarrow\; LiV_2O_5 + 3/4 \; CO_2$$
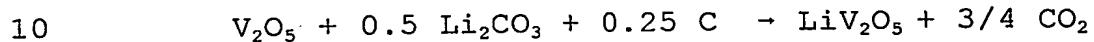
(a)   Pre-mix alpha $V_2O_5$, $Li_2CO_3$ and Shiwinigan Black
      (carbon) using ball mix with suitable media.
      Use a 25% weight excess of carbon over the
      reaction amounts above.   For example, according
      to reaction above:

|  | | |
|---|---|---|
| Need: | 1 mol $V_2O_5$ | 181.88g |
|  | 0.5 mol $Li_2CO_3$ | 36.95g |
|  | 0.25 mol carbon | 3.00g |

(but use 25% excess carbon → 3.75g)

(b)    Pelletize powder mixture

(c)    Heat pellet to 600°C in flowing argon (or other
       inert atmosphere) at a heat rate of
       approximately 2°/minute. Hold at 600°C for
5      about 60 minutes.

(d)    Allow to cool to room temperature in argon at
       cooling rate of about 2°/minute.

(e)    Powderize pellet using mortar and pestle

       This reaction is able to be conducted at a
10  temperature in a range of about 400°C to about 650°C in
    argon as shown, and also under other inert atmospheres
    such as nitrogen or vacuum. This reaction at this
    temperature range is primarily $C \rightarrow CO_2$. Note that the
    reaction $C \rightarrow CO$ primarily occurs at a temperature over
15  about 650°C (HT, high temperature); and the reaction $C \rightarrow$
    $CO_2$ primarily occurs at a temperature of under about
    650°C (LT, low temperature). The reference to about
    650°C is approximate and the designation "primarily"
    refers to the predominant reaction thermodynamically
20  favored although the alternate reaction may occur to some
    extent.

**EXAMPLE X**

Reaction 6.        Formation of $Li_3V_2(PO_4)_3$

$$V_2O_5 + 3/2\ Li_2CO_3 + 3\ (NH_4)_2HPO_4 + C \rightarrow Li_3V_2(PO_4)_3 + 2\ CO$$
25                  $$+ 3/2\ CO_2 + 6\ NH_3 + 9/2\ H_2O$$

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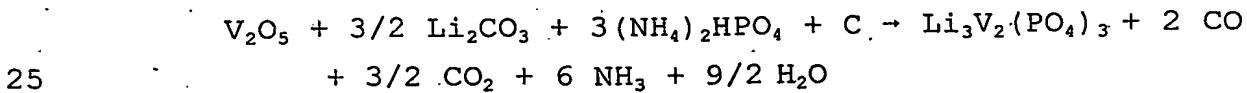
(a)   Pre-mix reactants above using ball mill with suitable media.   Use a 25% weight excess of carbon.   Thus,

|  |  |
|---|---|
| 1 mol $V_2O_5$ | 181.88g |
| 3/2 mol $Li_2CO_3$ | 110.84g |
| 3 mol $(NH_4)_2HPO_4$ | 396.18g |
| 1 mol carbon | 12.01g |

(but use 25% excess carbon → 15.01g)

(b)   Pelletize powder mixture

(c)   Heat pellet at 2°/minute to 300°C to remove $CO_2$ (from $Li_2CO_3$) and to remove $NH_3$, $H_2O$.   Heat in an inert atmosphere (e.g. argon).   Cool to room temperature.

(d)   Powderize and repelletize

(e)   Heat pellet in inert atmosphere at a rate of 2°C/minute to 850°C.   Dwell for 8 hours at 850°C

(f)   Cool to room temperature at a rate of 2°/minute in argon.

(e)   Powderize

This reaction is able to be conducted at a temperature in a range of about 700°C to about 950°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum.   A reaction temperature greater than about 670°C ensures C → CO reaction is primarily carried out.

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**Characterization of Active Materials
and Formation and Testing of Cells**

      Referring to **Figure 1,** the final product
$LiFePO_4$, prepared from $Fe_2O_3$ metal compound per Reaction

5    1(b), appeared brown/black in color. This olivine
material product included carbon that remained after
reaction. Its CuKα x-ray diffraction pattern contained
all of the peaks expected for this material as shown in
**Figure 1.** The pattern evident in **Figure 1** is consistent

10   with the single phase olivine phosphate, $LiFePO_4$. This
is evidenced by the position of the peaks in terms of the
scattering angle 2 θ (theta), x axis. The x-ray pattern
showed no peaks due to the presence of precursor oxides
indicating that the solid state reaction is essentially

15   entirely completed. Here the space group SG = pnma (62)
and the lattice parameters from XRD refinement are
consistent with the olivine structure. The values are a
= 10.2883Å (0.0020), b = 5.9759 (0.0037), c = 4.6717Å
(0.0012) 0.0072, cell volume = 287.2264Å³ (0.0685).

20   Density, p = 3.605 g/cc, zero = 0.452 (0.003). Peak at
full width half maximum, PFWHM = 0.21. Crystallite size
from XRD data = 704Å.

      The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula $LiFePO_4$.

25   The term "nominal formula" refers to the fact that the
relative proportion of atomic species may vary slightly
on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent, and that some portion
of P may be substituted by Si, S or As; and some portion

30   of O may be substituted by halogen, preferably F.

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The LiFePO$_4$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 19.0mg of active material. The positive electrode

5    contained, on a weight % basis, 85% active material, 10% carbon black, and 5% EPDM. The negative electrode was metallic lithium. The electrolyte was a 2:1 weight ratio mixture of ethylene carbonate and dimethyl carbonate within which was dissolved 1 molar LiPF$_6$. The cells were

10   cycled between about 2.5 and about 4.0 volts with performance as shown in **Figures 2 and 3.**

     **Figure 2** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon

15   about 19 milligrams of the LiFePO$_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is LiFePO$_4$. The lithium is extracted from the LiFePO$_4$ during charging of the cell. When fully

20   charged, about 0.72 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to Li$_{1-x}$FePO$_4$ where x appears to be equal to about 0.72, when the cathode material is at 4.0 volts versus Li/Li$^+$. The extraction represents

25   approximately 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 19 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the LiFePO$_4$. The re-insertion corresponds to approximately 121 milliamp

30   hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total

45

cumulative capacity demonstrated during the entire
extraction-insertion cycle is 244mAh/g.

Figure 3 presents data obtained by multiple
constant current cycling at 0.2 milliamp hours per square
5    centimeter of the $LiFePO_4$ versus lithium metal counter
electrode between 2.5 and 4.0 volts.  Data is shown for
two temperatures, 23°C and 60°C.  Figure 3 shows the
excellent rechargeability of the $LiFePO_4$ cell, and also
shows good cycling and capacity of the cell. The
10   performance shown after about 190 to 200 cycles is good
and shows that electrode formulation is very desirable.

Referring to Figure 4, there is shown data for
the final product $LiFe_{0.9}Mg_{0.1}PO_4$, prepared from the metal
compounds $Fe_2O_3$ and $Mg(OH)_2 \rightarrow Mg(OH)_2$, per Reaction 2(b).
15   Its CuKα x-ray diffraction pattern contained all of the
peaks expected for this material as shown in Figure 4.
The pattern evident in Figure 4 is consistent with the
single phase olivine phosphate compound, $LiFe_{0.9}Mg_{0.1}PO_4$.
This is evidenced by the position of the peaks in terms
20   of the scattering angle 2 θ (theta), x axis. The x-ray
pattern showed no peaks due to the presence of precursor
oxides indicating that the solid state reaction is
essentially entirely completed.  Here the space group SG
= Pnma (62) and the lattice parameters from XRD
25   refinement are consistent with the olivine structure.
The values are a = 10.2688Å (0.0069), b = 5.9709Å
(0.0072), c = 4.6762Å (0.0054), cell volume = 286.7208Å
(0.04294), p = 3.617 g/cc, zero = 0.702 (0.003), PFWHM =
0.01, and crystallite = 950Å.

30   The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula

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$LiFe_{0.9}Mg_{0.1}PO_4$. The term "nominal formula" refers to the
fact that the relative proportion of atomic species may
vary slightly on the order of 2 percent to 5 percent, or
more typically, 1 percent to 3 percent, and that some

5      substitution of P and O may be made while maintaining the
basic olivine structure.


       The $LiFe_{0.9}Mg_{0.1}PO_4$, prepared as described
immediately above, was tested in an electrochemical cell.
The positive electrode was prepared as described above,

10     using 18.9mg of active materials.  The positive
electrode, negative electrode and electrolyte were
prepared as described earlier and in connection with
**Figure 1.**  The cell was between about 2.5 and about 4.0
volts with performance as shown in **Figures 4, 5 and 6**.


15            **Figure 5** shows the results of the first
constant current cycling at 0.2 milliamps per square
centimeter between about 2.5 and 4.0 volts based upon
about 18.9 milligrams of the $LiFe_{0.9}Mg_{0.1}PO_4$ active
material in the cathode (positive electrode).  In an as

20     prepared, as assembled, initial condition, the positive
electrode active material is $LiFe_{0.9}Mg_{0.1}PO_4$.  The lithium
is extracted from the $LiFe_{0.9}Mg_{0.1}PO_4$ during charging of
the cell.  When fully charged, about 0.87 units of
lithium have been removed per formula unit.

25     Consequently, the positive electrode active material
corresponds to $Li_{1-x}Fe_{0.9}Mg_{0.1}PO_4$ where x appears to be equal
to about 0.87, when the cathode material is at 4.0 volts
versus $Li/Li^+$.  The extraction represents approximately
150 milliamp hours per gram corresponding to about 2.8

30     milliamp hours based on 18.9 milligrams active material.
Next, the cell is discharged whereupon a quantity of
lithium is re-inserted into the $LiFe_{0.9}Mg_{0.1}PO_4$ .  The re-

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insertion corresponds to approximately 146 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 296 mAhr/g. This material has a much better cycle profile than the $LiFePO_4$. **Figure 5** ($LiFe_{0.9}Mg_{0.1}PO_4$) shows a very well defined and sharp peak at about 150 mAh/g. In contrast, **Figure 2** ($LiFePO_4$) shows a very shallow slope leading to the peak at about 123 mAh/g. The Fe-phosphate **(Figure 2)** provides 123 mAh/g compared to its theoretical capacity of 170 mAh/g. This ratio of 123/170, 72% is relatively poor compared to the Fe/Mg-phosphate. The Fe/Mg-phosphate **(Figure 5)** provides 150 mAh/g compared to a theoretical capacity of 160, a ratio of 150/160 or 94%.

**Figure 6** presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the $LiFe_{0.9}Mg_{0.1}PO_4$ versus lithium metal counter electrode between 2.5 and 4.0 volts. **Figure 6** shows the excellent rechargeability of the $Li/LiFe_{0.9}Mg_{0.1}PO_4$ cell, and also shows good cycling and capacity of the cell. The performance shown after about 150 to 160 cycles is very good and shows that electrode formulation $LiFe_{0.9}Mg_{0.1}PO_4$ performed significantly better than the $LiFePO_4$. Comparing **Figure 3** ($LiFePO_4$) to **Figure 6** ($LiFe_{0.9}Mg_{0.1}PO_4$) it can be seen that the Fe/Mg-phosphate maintains its capacity over prolonged cycling, whereas the Fe-phosphate capacity fades significantly.

**Figure 7** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 16 milligrams of the $LiFe_{0.8}Mg_{0.2}PO_4$ active material

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in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Mg_{0.2}PO_4$. The lithium is extracted from the $LiFe_{0.8}Mg_{0.2}PO_4$ during charging of the

5      cell. When fully charged, about 0.79 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $LiFe_{0.8}Mg_{0.2}PO_4$ where x appears to be equal to about 0.79, when the cathode material is at 4.0 volts versus $Li/Li^+$.

10     The extraction approximately 140 milliamp hours per gram corresponding to about 2.2 milliamp hours based on 16 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Mg_{0.2}PO_4$. The re-insertion corresponds to

15     approximately 122 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 262 mAhr/g.

20          Referring to **Figure 8**, there is shown data for the final product $LiFe_{0.9}Ca_{0.1}PO_4$, prepared from $Fe_2O_3$ and $Ca(OH)_2$ by Reaction 3. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 8**. The pattern evident in

25     **Figure 8** is consistent with the single phase olivine phosphate compound, $LiFe_{0.9}Ca_{0.1}PO_4$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating

30     that the solid state reaction is essentially entirely completed. Here the space group SG = Pnma (62) and the lattice parameters from XRD refinement are consistent with olivine. The values are a = 10.3240Å (0.0045), b =

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6.0042Å (0.0031), c = 4.6887Å (0.0020), cell volume = 290.6370Å (0.1807), zero = 0.702 (0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite = 680Å. The x-ray pattern demonstrates that the product of the invention was indeed

5    the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.


**Figure 9** shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.5 milligrams of the $LiFe_{0.8}Ca_{0.2}PO_4$ active

10   material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Ca_{0.2}PO_4$. The lithium is extracted from the $LiFe_{0.8}Ca_{0.2}PO_4$ during charging of the cell. When fully charged, about 0.71 units of

15   lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $LiFe_{0.8}Ca_{0.2}PO_4$ where x appears to be equal to about 0.71, when the cathode material is at 4.0 volts versus $Li/Li^+$. The extraction represents approximately

20   123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 18.5 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Ca_{0.2}PO_4$. The re-insertion corresponds to approximately 110 milliamp hours

25   per gram proportional to the insertion of nearly all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total specific cumulative capacity over the entire cycle is 233 mAhr/g.


**Figure 10** shows the results of the first

30   constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the $LiFe_{0.8}Zn_{0.2}PO_4$ olivine active

50

material in the cathode (positive electrode). In an as
prepared, as assembled, initial condition, the positive
electrode active material is $LiFe_{0.8}Zn_{0.2}PO_4$, prepared from
$Fe_2O_3$ and $Zn_3(PO_4)_2$ by Reaction 4. The lithium is.
5     extracted from the $LiFe_{0.8}Zn_{0.2}PO_4$ during charging of the
cell. When fully charged, about 0.74 units of lithium
have been removed per formula unit. Consequently, the
positive electrode active material corresponds to $Li_{1-}$
$_xFe0.8Zn0.2PO4$ where x appears to be equal to about 0.74,
10    when the cathode material is at 4.0 volts versus $Li/Li^+$.
The extraction represents approximately 124 milliamp
hours per gram corresponding to about 2.3 milliamp hours
based on 18.9 milligrams active material. Next, the cell
is discharged whereupon a quantity of lithium is re-
15    inserted into the $LiFe_{0.8}Zn_{0.2}PO_4$. The re-insertion
corresponds to approximately 108 milliamp hours per gram
proportional to the insertion of nearly all of the
lithium. The bottom of the curve corresponds to
approximately 2.5 volts.

20              Referring to **Figure 11**, the final product
$LiV_2O_5$, prepared by Reaction 5, appeared black in color.
Its CuKα x-ray diffraction pattern contained all of the
peaks expected for this material as shown in **Figure 11**.
The pattern evident in **Figure 11** is consistent with a
25    single oxide compound gamma-$LiV_2O_5$. This is evidenced by
the position of the peaks in terms of the scattering
angle 2 θ (theta), x axis. The x-ray pattern showed no
peaks due to the presence of precursor oxides indicating
that the solid state reaction is essentially entirely
30    completed.

              The x-ray pattern demonstrates that the product
of the invention was indeed the nominal formula gamma-

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$LiV_2O_5$. The term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent.

5          The $LiV_2O_5$ prepared as described immediately
above, was tested in an electrochemical cell. The cell
was prepared as described above and cycled with
performance as shown in **Figures 12 and 13**.

          **Figure 12** shows the results of the first
10    constant current cycling at 0.2 milliamps per square
centimeter between about 2.8 and 3.8 volts based upon
about 15.0 milligrams of the $LiV_2O_5$ active material in
the cathode (positive electrode). In an as prepared, as
assembled, initial condition, the positive electrode
15    active material is $LiV_2O_5$. The lithium is extracted from
the $LiV_2O_5$ during charging of the cell. When fully
charged, about 0.93 unit of lithium had been removed per
formula unit. Consequently, the positive electrode
active material corresponds to $Li_{1-x}V_2O_5$ where x appears to
20    be equal to about 0.93, when the cathode material is at
3.8 volts versus $Li/Li^+$. The extraction represents
approximately 132 milliamp hours per gram corresponding
to about 2.0 milliamp hours based on 15.0 milligrams
active material. Next, the cell is discharged whereupon
25    a quantity of lithium is re-inserted into the $LiV_2O_5$. The
re-insertion corresponds to approximately 130 milliamp
hours per gram proportional to the insertion of
essentially all of the lithium. The bottom of the curve
corresponds to approximately 2.8 volts.

30          **Figure 13** presents data obtained by multiple
constant current cycling at 0.4 milliamp hours per square

52

centimeter (C/2 rate) of the $LiV_2O_5$ versus lithium metal
counter electrode between 3.0 and 3.75 volts. Data for
two temperature conditions are shown, 23°C and 60°C.
**Figure 13** is a two part graph with **Figure 13A** showing the
5       excellent rechargeability of the $LiV_2O_5$. **Figure 13B**
shows good cycling and capacity of the cell. The
performance shown up to about 300 cycles is good.

Referring to **Figure 14**, the final product
$Li_3V_2(PO_4)_3$, prepared by Reaction 6, appeared green/black
10      in color. Its CuKα x-ray diffraction pattern contained
all of the peaks expected for this material as shown in
**Figure 14**. The pattern evident in **Figure 14** is
consistent with a single phosphate compound $Li_3V_2(PO_4)_3$ of
the monoclinic, Nasicon phase. This is evidenced by the
15      position of the peaks in terms of the scattering angle 2
θ (theta), x axis. The x-ray pattern showed no peaks due
to the presence of precursor oxides indicating that the
solid state reaction is essentially entirely completed.

The x-ray pattern demonstrates that the product
20      of the invention was indeed the nominal formula
$Li_3V_2(PO_4)_3$. The term "nominal formula" refers to the fact
that the relative proportion of atomic species may vary
slightly on the order of 2 percent to 5 percent, or more
typically, 1 percent to 3 percent; and that substitution
25      of P and O may occur.

The $Li_3V_2(PO_4)_3$ prepared as described immediately
above, was tested in an electrochemical cell. The cell
was prepared as described above, using 13.8mg of active
material. The cell was prepared as described above and
30      cycled between about 3.0 and about 4.2 volts using the
EVS technique with performance as shown in **Figures 16 and**

17. **Figure 16** shows specific capacity versus electrode potential against Li.  **Figure 17** shows differential capacity versus electrode potential against Li.

5    A comparative method was used to form $Li_3V_2(PO_4)_3$.  Such method was reaction without carbon and under $H_2$-reducing gas as described in U.S. Patent No. 5,871,866.  The final product, prepared as per U.S. Patent No. 5,871,866, appeared green in color.  Its $CuK\alpha$ x-ray diffraction pattern contained all of the peaks
10   expected for this material as shown in **Figure 15**.  The pattern evident in **Figure 15** is consistent with a monoclinic Nasicon single phase phosphate compound $Li_3V_2(PO_4)_3$.  This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the
15   presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Chemical analysis for lithium and vanadium by atomic absorption spectroscopy showed, on a percent by weight
20   basis, 5.17 percent lithium and 26 percent vanadium. This is close to the expected result of 5.11 percent lithium and 25 percent vanadium.

     The chemical analysis and x-ray patterns of **Figures 14 and 15** demonstrate that the product of **Figure**
25   **14** was the same as that of **Figure 15**.  The product of **Figure 14** was prepared without the undesirable $H_2$ atmosphere and was prepared by the novel carbothermal solid state synthesis of the invention.

     **Figure 16** shows a voltage profile of the test
30   cell, based on the $Li_3V_2(PO_4)_3$ positive electrode active material made by the process of the invention and as

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characterized in **Figure 14**. It was cycled against a
lithium metal counter electrode. The data shown in
**Figure 16** is based on the Electrochemical Voltage
Spectroscopy (EVS) technique. Electrochemical and
5    kinetic data were recorded using the Electrochemical
Voltage Spectroscopy (EVS) technique. Such technique is
known in the art as described by J. Barker in Synth, Met
28, D217 (1989); Synth. Met. 32, 43 (1989); J. Power
Sources, 52, 185 (1994); and Electrochemica Acta, Vol.
10   40, No. 11, at 1603 (1995). **Figure 16** clearly shows and
highlights the reversibility of the product. The positive
electrode contained about 13.8 milligrams of the
$Li_3V_2(PO_4)_3$ active material. The positive electrode
showed a performance of about 133 milliamp hours per gram
15   on the first discharge. In **Figure 16**, the capacity in,
and the capacity out are essentially the same, resulting
in essentially no capacity loss. **Figure 17** is an EVS
differential capacity plot based on **Figure 16**. As can be
seen from **Figure 17**, the relatively symmetrical nature of
20   peaks indicates good electrical reversibility, there are
small peak separations (charge/discharge), and good
correspondence between peaks above and below the zero
axis. There are essentially no peaks that can be related
to irreversible reactions, since all peaks above the axis
25   (cell charge) have corresponding peaks below the axis
(cell discharge), and there is essentially no separation
between the peaks above and below the axis. This shows
that the carbothermal method of the invention produces
high quality electrode material.

30      **Figure 18** presents data obtained by multiple
constant current cycling at 0.2 milliamp hours per square
centimeter of the $LiFe_{0.8}Mg_{0.2}PO_4$ versus lithium metal
counter electrode between 2.5 and 4.0 volts. **Figure 18**

shows the excellent rechargeability of the
$Li/LiFe_{0.8}Mg_{0.2}PO_4$ cell, and also shows good cycling and
capacity of the cell.  The performance shown after about
110 to 120 cycles at 23°C is very good and shows that

5    electrode formulation $LiFe_{0.8}Mg_{0.2}PO_4$ performed
significantly better than the $LiFePO_4$.  The cell cycling
test at 60°C was started after the 23°C test and was
ongoing.  Comparing **Figure 3** ($LiFePO_4$) to **Figure 18**
($LiFe_{0.8}Mg_{0.2}PO_4$), it can be seen that the Fe/Mg-phosphate

10   maintains its capacity over prolonged cycling, whereas
the Fe-phosphate capacity fades significantly.

In addition to the above cell tests, the active
materials of the invention were also cycled against
insertion anodes in non-metallic, lithium ion, rocking

15   chair cells.

The lithium mixed metal phosphate and the
lithium metal oxide were used to formulate a cathode
electrode.  The electrode was fabricated by solvent
casting a slurry of the treated, enriched lithium

20   manganese oxide, conductive carbon, binder, plasticizer
and solvent.  The conductive carbon used was Super P (MMM
Carbon).  Kynar Flex 2801® was used as the binder and
electronic grade acetone was used as a solvent.  The
preferred plasticizer was dibutyl phthalate (DPB).  The

25   slurry was cast onto glass and a free-standing electrode
was formed as the solvent was evaporated.  In this
example, the cathode had 23.1mg $LiFe_{0.9}Mg_{0.1}PO_4$ active
material.  Thus, the proportions are as follows on a
percent weight basis: 80% active material; 8% Super P

30   carbon; and 12% Kynar binder.

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A graphite counter electrode was prepared for
use with the aforesaid cathode. The graphite counter
electrode served as the anode in the electrochemical
cell. The anode had 10.8 mg of the MCMB graphite active
5    material. The graphite electrode was fabricated by
solvent casting a slurry of MCMB2528 graphite, binder,
and casting solvent. MCMB2528 is a mesocarbon microbead
material supplied by Alumina Trading, which is the U.S.
distributor for the supplier, Osaka Gas Company of Japan.
10   This material has a density of about 2.24 grams per cubic
centimeter; a particle size maximum for at least 95% by
weight of the particles of 37 microns; median size of
about 22.5 microns and an interlayer distance of about
0.336. As in the case of the cathode, the binder was a
15   copolymer of polyvinylidene difluoride (PVdF) and
hexafluoropropylene (HFP) in a wt. ratio of PVdF to HFP
of 88:12. This binder is sold under the designation of
Kynar Flex 2801®, showing it's a registered trademark.
Kynar Flex is available from Atochem Corporation. An
20   electronic grade solvent was used. The slurry was cast
onto glass and a free standing electrode was formed as
the casting solvent evaporated. The electrode
composition was approximately as follows on a dry weight
basis: 85% graphite; 12% binder; and 3% conductive
25   carbon.

A rocking chair battery was prepared comprising
the anode, the cathode, and an electrolyte. The ratio of
the active cathode mass to the active anode mass was
about 2.14:1. The two electrode layers were arranged
30   with an electrolyte layer in between, and the layers were
laminated together using heat and pressure as per the
Bell Comm. Res. patents incorporated herein by reference
earlier. In a preferred method, the cell is activated

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with EC/DMC solvent in a weight ratio of 2:1 in a
solution containing 1 M $LiPF_6$ salt.

   **Figures 19** and **20** show data for the first four
complete cycles of the lithium ion cell having the
5  $LiFe_{0.9}Mg_{0.1}PO_4$ cathode and the MCMB2528 anode. The cell
comprised 23.1mg active $LiFe_{0.9}Mg_{0.1}PO_4$ and 10.8mg active
MCMB2528 for a cathode to anode mass ratio of 2.14. The
cell was charged and discharged at 23°C at an approximate
C/10 (10 hour) rate between voltage limits of 2.50 V and
10  3.60 V. The voltage profile plot **(Figure 19)** shows the
variation in cell voltage versus time for the
$LiFe_{0.9}Mg_{0.1}PO_4$/MCMB2528 lithium ion cell. The symmetrical
nature of the charge-discharge is clearly evident. The
small degree of voltage hysteresis between the charge and
15  discharge processes is evidence for the low overvoltage
in the system, which is very good. **Figure 20** shows the
variation of $LiFe_{0.9}Mg_{0.1}PO_4$ specific capacity with cycle
number. Clearly, over the cycles shown, the material
demonstrates good cycling stability.

20    **Figure 21** shows data for the first three
complete cycles of the lithium ion cell having the gamma-
$LiV_2O_5$ cathode and the MCMB2528 anode. The cell prepared
was a rocking chair, lithium ion cell as described above.
The cell comprised 29.1mg gamma-$LiV_2O_5$ cathode active
25  material and 12.2mg MCMB2528 anode active material, for a
cathode to anode mass ratio of 2.39. As stated earlier,
the liquid electrolyte used was EC/DMC (2:1) and 1M
$LiPF_6$. The cell was charged and discharged at 23°C at an
approximate C/10 (10 hour) rate between voltage limits of
30  2.50 V and 3.65 V. The voltage profile plot **(Figure 21)**
shows the variation in cell voltage versus time for the
$LiV_2O_5$/MCMB2528 lithium ion cell. The symmetrical nature

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of the charge-discharge is clearly evident.  The small
degree of voltage hysteresis between the charge and
discharge processes is evidence for the low overvoltage
in the system, which is very good.

5.

In summary, the invention provides new
compounds $Li_aMI_bMII_c(PO_4)_d$ and gamma-$LiV_2O_5$ by new methods
which are adaptable to commercial scale production.  The
$Li_1MI_{1-y}MII_yPO_4$ compounds are isostructural olivine

10    compounds as demonstrated by XRD analysis.  Substituted
compounds, such as $LiFe_{1-y}Mg_yPO_4$ show better performance
than $LiFePO_4$ unsubstituted compounds when used as
electrode active materials.  The method of the invention
utilizes the reducing capabilities of carbon along with

15    selected precursors and reaction conditions to produce
high quality products suitable as electrode active
materials or as ion conductors.  The reduction capability
of carbon over a broad temperature range is selectively
applied along with thermodynamic and kinetic

20    considerations to provide an energy-efficient, economical
and convenient process to produce compounds of a desired
composition and structure.  This is in contrast to known
methods.

Principles of carbothermal reduction have been
25    applied to produce pure metal from metal oxides by
removal of oxygen.  See, for example, U.S. Patent Nos.
2,580,878, 2,570,232, 4,177,060, and 5,803,974.
Principles of carbothermal and thermal reduction have
also been used to form carbides.  See, for example, U.S.
30    Patent Nos. 3,865,745 and 5,384,291; and non-oxide
ceramics (see U.S. Patent No. 5,607,297).  Such methods
are not known to have been applied to form lithiated
products or to form products without oxygen abstraction

from the precursor. The methods described with respect to
the present invention provide high quality products which
are prepared from precursors which are lithiated during
the reaction without oxygen abstraction. This is a
surprising result. The new methods of the invention also
provide new compounds not known to have been made before.

For example, alpha-$V_2O_5$ is conventionally
lithiated electrochemically against metallic lithium.
Thus, alpha-$V_2O_5$ is not suitable as a source of lithium
for a cell. As a result, alpha-$V_2O_5$ is not used in an
ion cell. In the present invention, alpha-$V_2O_5$ is
lithiated by carbothermal reduction using a simple
lithium-containing compound and the reducing capability
of carbon to form a gamma-$LiV_2O_5$. The single phase
compound, gamma-$LiV_2O_5$ is not known to have been directly
and independently prepared before. There is not known to
be a direct synthesis route. Attempts to form it as a
single phase resulted in a mixed phase product containing
one or more beta phases and having the formula $Li_xV_2O_5$
with $0 < x \le 0.49$. This is far different from the
present single phase gamma-$Li_xV_2O_5$ with x equal to one, or
very close to one. The flexibility of the process of the
present invention is such that it can be conducted over a
wide temperature range. The higher the temperature, the
more quickly the reaction proceeds. For example, at
650°C, conversion of alpha-$V_2O_5$ to gamma-$LiV_2O_5$ occurs in
about one hour, and at 500° it takes about 8 hours.
Here, about one quarter (1/4) atomic unit of carbon is
used to reduce one atomic unit of vanadium, that is,
$V^{+5}V^{+5}$ to $V^{+5}V^{+4}$. The predominate reaction is C to $CO_2$
where for each atomic unit of carbon at ground state
zero, a plus 4 oxidation state results. Correspondingly,
for each 1/4 atomic unit of carbon, one atomic unit of

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vanadium is reduced from $V^{+5}$ to $V^{+4}$. (See Reaction 5).
The new product, gamma-$LiV_2O_5$ is air-stable and suitable
as an electrode material for an ion cell or rocking chair
battery.

5          The convenience and energy efficiency of the
present process can also be contrasted to known methods
for forming products under reducing atmosphere such as $H_2$
which is difficult to control, and from complex and
expensive precursors. In the present invention, carbon
10    is the reducing agent, and simple, inexpensive and even
naturally occurring precursors are useable. For example,
it is possible to produce $LiFePO_4$ from $Fe_2O_3$, a simple
common oxide. (See Reaction 1b). The production of
$LiFePO_4$ provides a good example of the thermodynamic and
15    kinetic features of the method. Iron phosphate is
reduced by carbon and lithiated over a broad temperature
range. At about 600°C, the C to $CO_2$ reaction
predominates and takes about a week to complete. At
about 750°C, the C to CO reaction predominates and takes
20    about 8 hours to complete. The C to $CO_2$ reaction
requires less carbon reductant but takes longer due to
the low temperature kinetics. The C to CO reaction
requires about twice as much carbon, but due to the high
temperature reaction kinetics, it proceeds relatively
25    fast. In both cases, the Fe in the precursor $Fe_2O_3$ has
oxidation state +3 and is reduced to oxidation (valence)
state +2 in the product $LiFePO_4$. The C to CO reaction
requires that ½ atomic unit of carbon be used for each
atomic unit of Fe reduced by one valence state. The CO
30    to $CO_2$ reaction requires that 1/4 atomic unit of carbon
be used for each atomic unit of Fe reduced by one valence
state.

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         The active materials of the invention are also
characterized by being stable in an as-prepared
condition, in the presence of air and particularly humid
air.  This is a striking advantage, because it
5    facilitates preparation of and assembly of battery
cathodes and cells, without the requirement for
controlled atmosphere.  This feature is particularly
important, as those skilled in the art will recognize
that air stability, that is, lack of degradation on
10   exposure to air, is very important for commercial
processing.  Air-stability is known in the art to more
specifically indicate that a material does not hydrolyze
in presence of moist air.  Generally, air-stable
materials are also characterized by Li being extracted
15   therefrom above about 3.0 volts versus lithium.  The
higher the extraction potential, the more tightly bound
the lithium ions are to the host lattice.  This tightly
bound property generally confers air stability on the
material.  The air-stability of the materials of the
20   invention is consistent with the stability demonstrated
by cycling at the conditions stated herein.  This is in
contrast to materials which insert Li at lower voltages,
below about 3.0 volts versus lithium, and which are not
air-stable, and which hydrolyze in moist air.


25        While this invention has been described in
terms of certain embodiments thereof, it is not intended
that it be limited to the above description, but rather
only to the extent set forth in the following claims.


          The embodiments of the invention in which an
30   exclusive property or privilege is claimed are defined in
the following claims.

**What Is Claimed Is:**

1.   A compound represented by the nominal general formula $LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least one selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

2.   The compound of claim 1 where $0 < y \leq 0.2$.

3.   The compound of claim 1 having the nominal formula $LiFe_{1-y}Mg_yPO_4$.

4.   The compound of claim 1 having the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$.

5.   The compound of claim 1 having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

6.   The compound of claim 1 having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

7.   The compound of claim 1 having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

8.   The compound of claim 1 having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

9.   The compound of claim 1 which has an olivine structure.

10.   A compound having the nominal general formula $LiMI_{1-y}MII_yPO_4$ where MI is selected from the group

consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and
mixtures thereof, and MII is selected from the group
consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and
mixtures thereof, and where y is greater than zero and
less than one.

11.  An olivine compound having the nominal
general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one
transition metal selected from Groups 4 to 11 inclusive
of the Periodic Table and has a +2 valence state, MII is
at least one metallic element which is selected from
Groups 2, 12, and 14 of the Periodic Table and has a +2
valence state, and where
$0 < y < 1$.

12.  The compound of claim 11 wherein MI is
selected from the group consisting of V, Cr, Mn, Fe, Co,
Cu, and mixtures thereof.

13.  The compound of claim 11 wherein MII is
selected from the group consisting of Mg, Ca, Ba, Zn, and
mixtures thereof.

14.  An electrode comprising a binder, an
electrically conductive carbonaceous material, and an
active material represented by the nominal general
formula $LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least
one selected from the group consisting of Mg, Ca, Zn, Sr,
Pb, Cd, Sn, Ba, Be, and mixtures thereof.

15.  The electrode of claim 14 wherein said
active material is a compound where $0 < y \leq 0.2$.

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16. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Mg_yPO_4$.

17. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$.

18. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

19. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

20. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

21. The electrode of claim 14 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

22. The electrode of claim 14 wherein said active material has an olivine structure.

23. An electrode comprising a binder, an electrically conductive carbonaceous material and an active material which is an olivine compound represented by the nominal general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one transition metal selected from Groups 4 to 11 inclusive of the Periodic Table and has a +2 valence state, MII is at least one metallic element which is

selected from Groups 2, 12, and 14 of the Periodic Table and has a +2 valence state, and where $0 < y < 1$.

24. The electrode of claim 23 wherein MI is selected from the group consisting of V, Cr, Mn, Fe, Co, Cu, and mixtures thereof.

25. The electrode of claim 23 wherein MII is selected from the group consisting of Mg, Ca, Ba, Zn, and mixtures thereof.

26. A lithium ion battery comprising:

a first electrode having an active material represented by the nominal general formula $LiFe_{1-y}M_yPO_4$ where $0 < y < 0.5$ and M is at least one selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof;

a second electrode which is a counter-electrode to said first electrode; and

an electrolyte between said electrodes.

27. The battery of claim 26 wherein said active material is a compound where $0 < y \leq 0.2$.

28. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Mg_yPO_4$.

29. The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$.

30.   The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Ca_yPO_4$.

31.   The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

32.   The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{1-y}Zn_yPO_4$.

33.   The battery of claim 26 wherein said active material is a compound having the nominal formula $LiFe_{0.9}Zn_{0.1}PO_4$.

34.   The battery of claim 26 wherein said active material has an olivine structure.

35.   A lithium ion battery comprising:

a first electrode having an active material which is an olivine compound represented by the nominal general formula $LiMI_{1-y}MII_yPO_4$ where MI is at least one transition metal selected from Groups 4 to 11 inclusive of the Periodic Table and has a +2 valence state, MII is at least one metallic element which is selected from Groups 2, 12, and 14 of the Periodic Table and has a +2 valence state, and where $0 < y < 1$;

a second electrode which is a counter-electrode to said first electrode; and

an electrolyte between said electrodes.

36.  The battery of claim 35 wherein MI is selected from the group consisting of V, Cr, Mn, Fe, Co, Cu, and mixtures thereof.

37.  The battery of claim 35 wherein MII is selected from the group consisting of Mg, Ca, Ba, Zn, and mixtures thereof.

38.  A compound represented by the nominal formula $LiV_2O_5$ and having an orthorhombic crystal structure with a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å and c = 10.6 ± 0.2Å.

39.  The compound of claim 38 which is prepared by reacting vanadium pentoxide and lithium compound in the presence of carbon at an elevated temperature sufficient to form said single phase compound.

40.  An electrode comprising a binder, an electrically conductive carbonaceous material and an active material which is a compound represented by the nominal general formula $LiV_2O_5$ and having an orthorhombic crystal structure with a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å and c = 10.6 ± 0.2Å.

41.  A lithium ion battery comprising:
        a first electrode having an active material which is a compound represented by the nominal formula $LiV_2O_5$ and having orthorhombic crystal structure which a = 9.7 ± 0.2Å, b = 3.6 ± 0.2Å and c = 10.6 ± 0.2Å;
        a second electrode which is a counter-electrode to said first electrode; and
        an electrolyte between said electrodes.
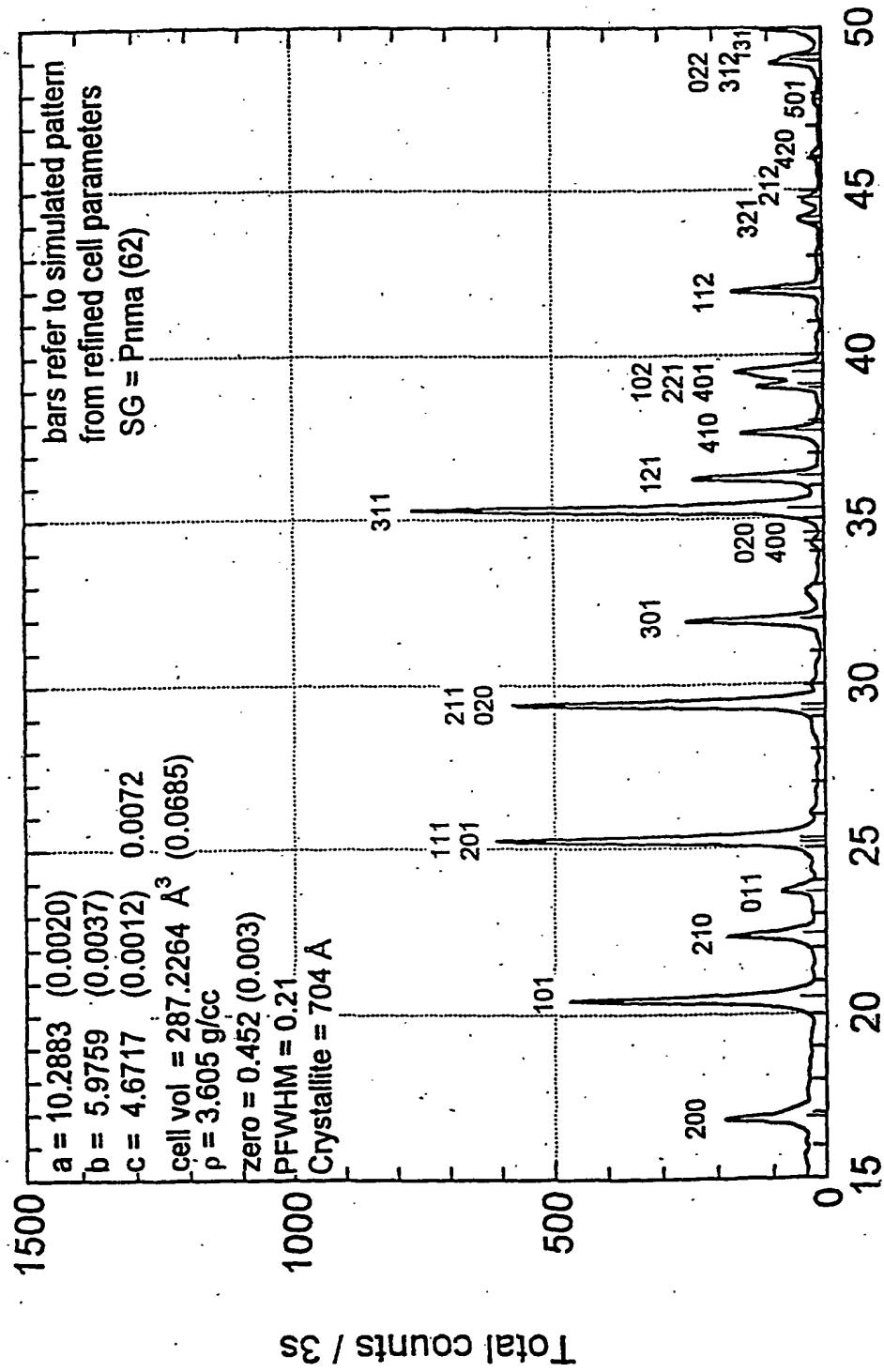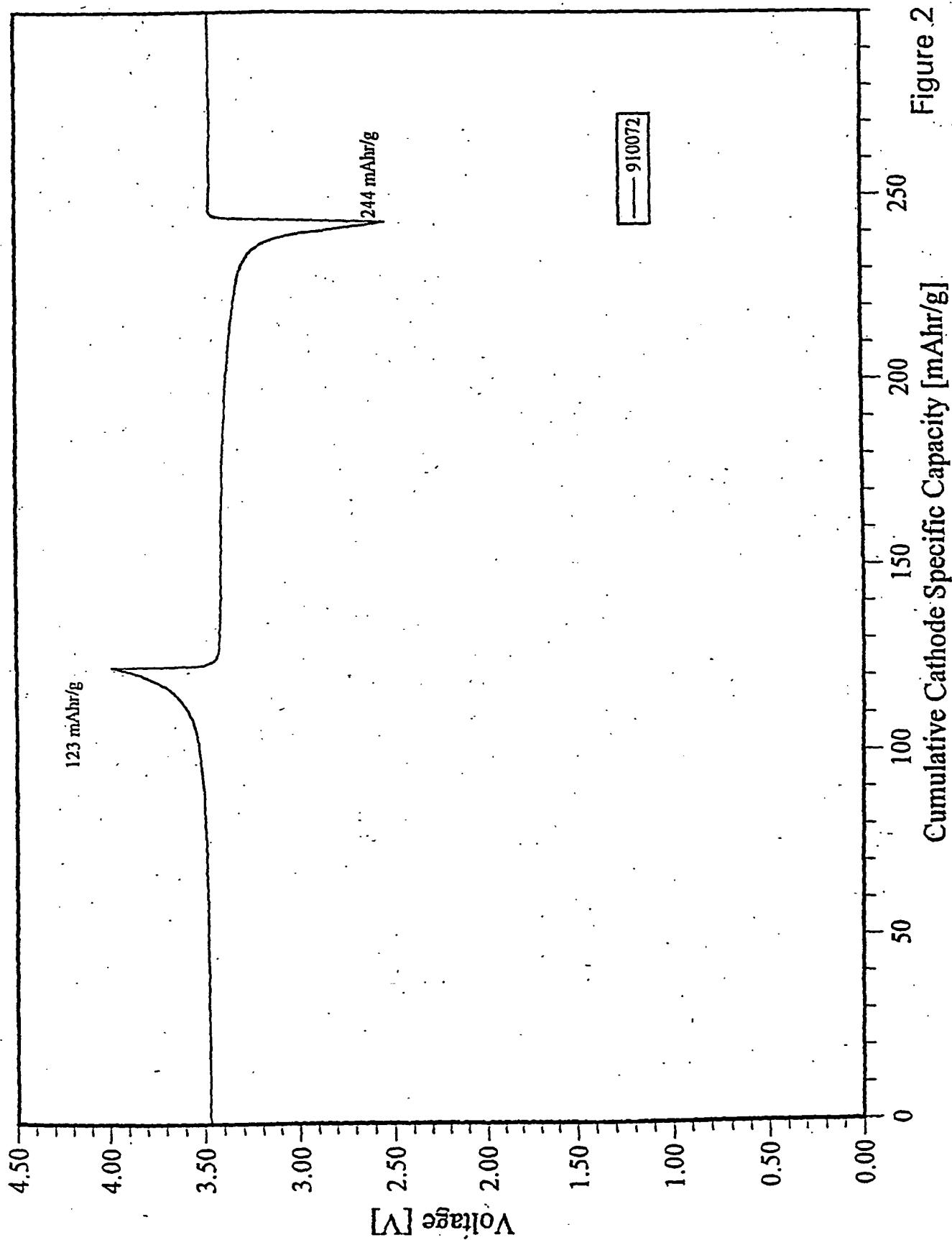
Figure 1

LiFePO4  2.5 – 4.0 V
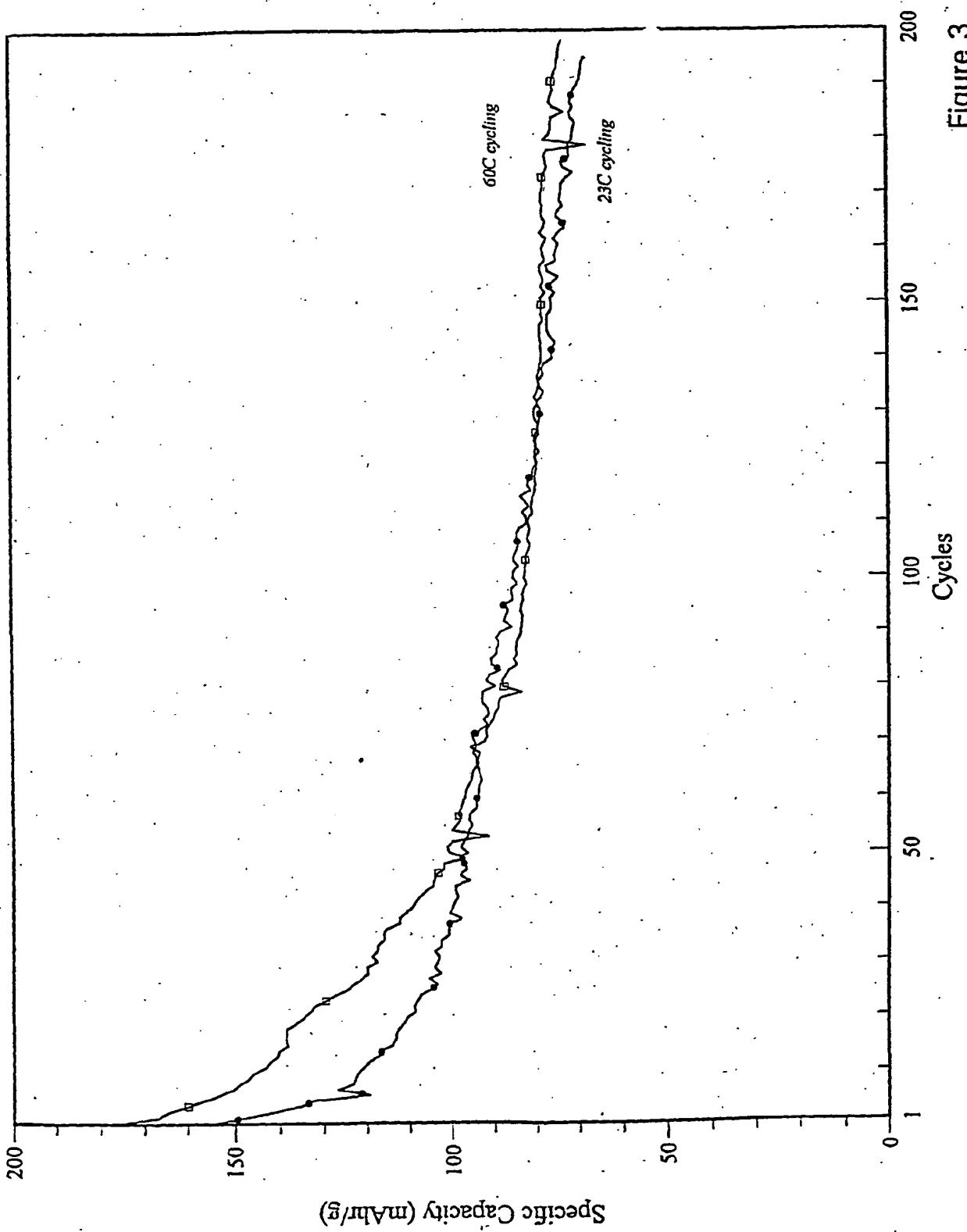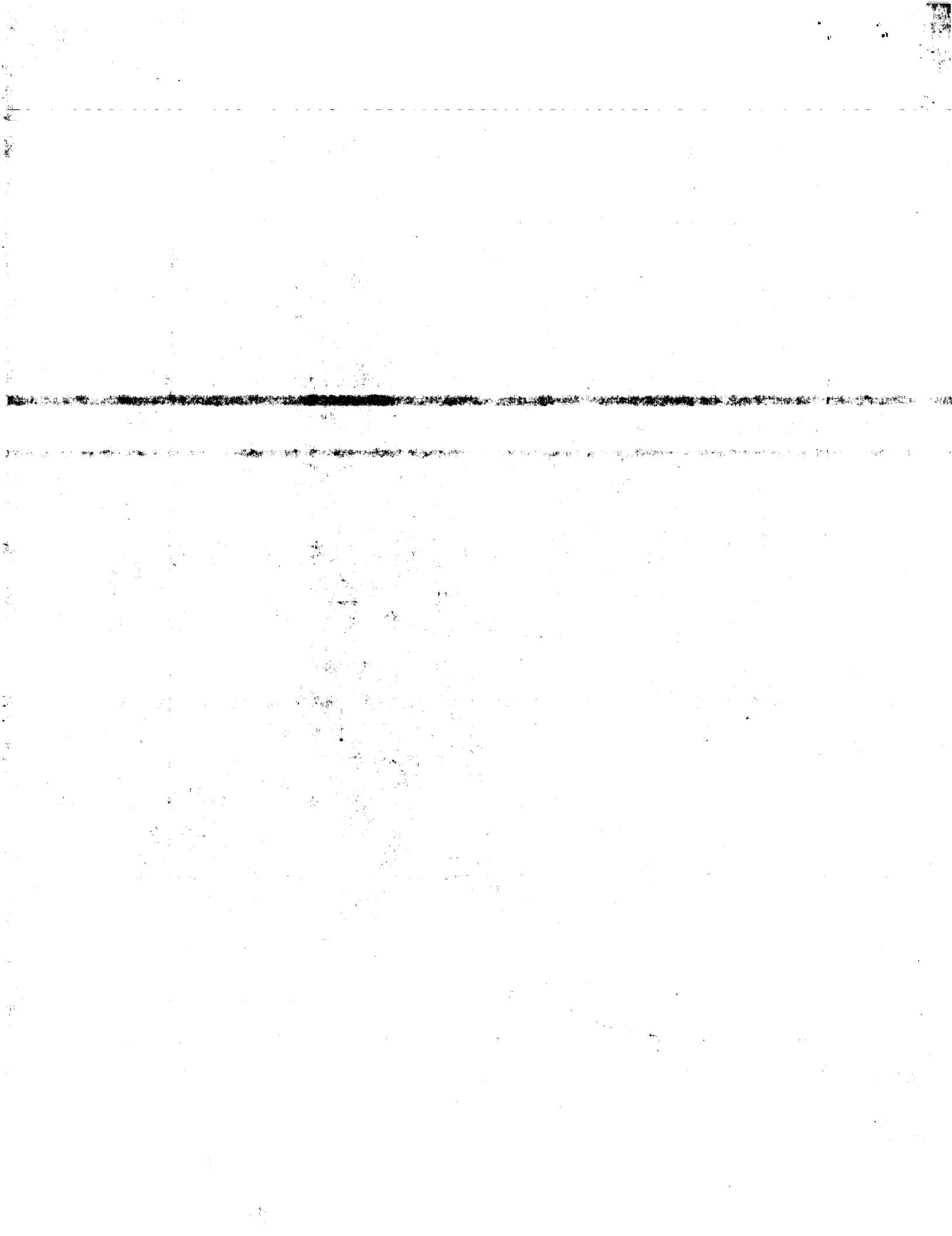
Figure 2

Figure 3

1S0937A1 (LiFe$_{0.9}$Mg$_{0.1}$PO$_4$)

bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)

a = 10.2688   (0.0069)
b = 5.9709    (0.0072)
c = 4.6762    (0.0054)

cell vol 286.7208Å$^3$   0.04294
ρ = 3.617 g/cc
zero = 0.702 (0.003)
PFWHM = 0.19
Crystallite = 950 Å

Total counts / 2s

2-Theta / (°)

Figure 4

LiFe0.9Mg0.1PO4  2.5 - 4.0 V

150 mAhr/g

296 mAhr/g

910310

Cumulative Cathode Specific Capacity [mAhr/g]

Voltage [V]
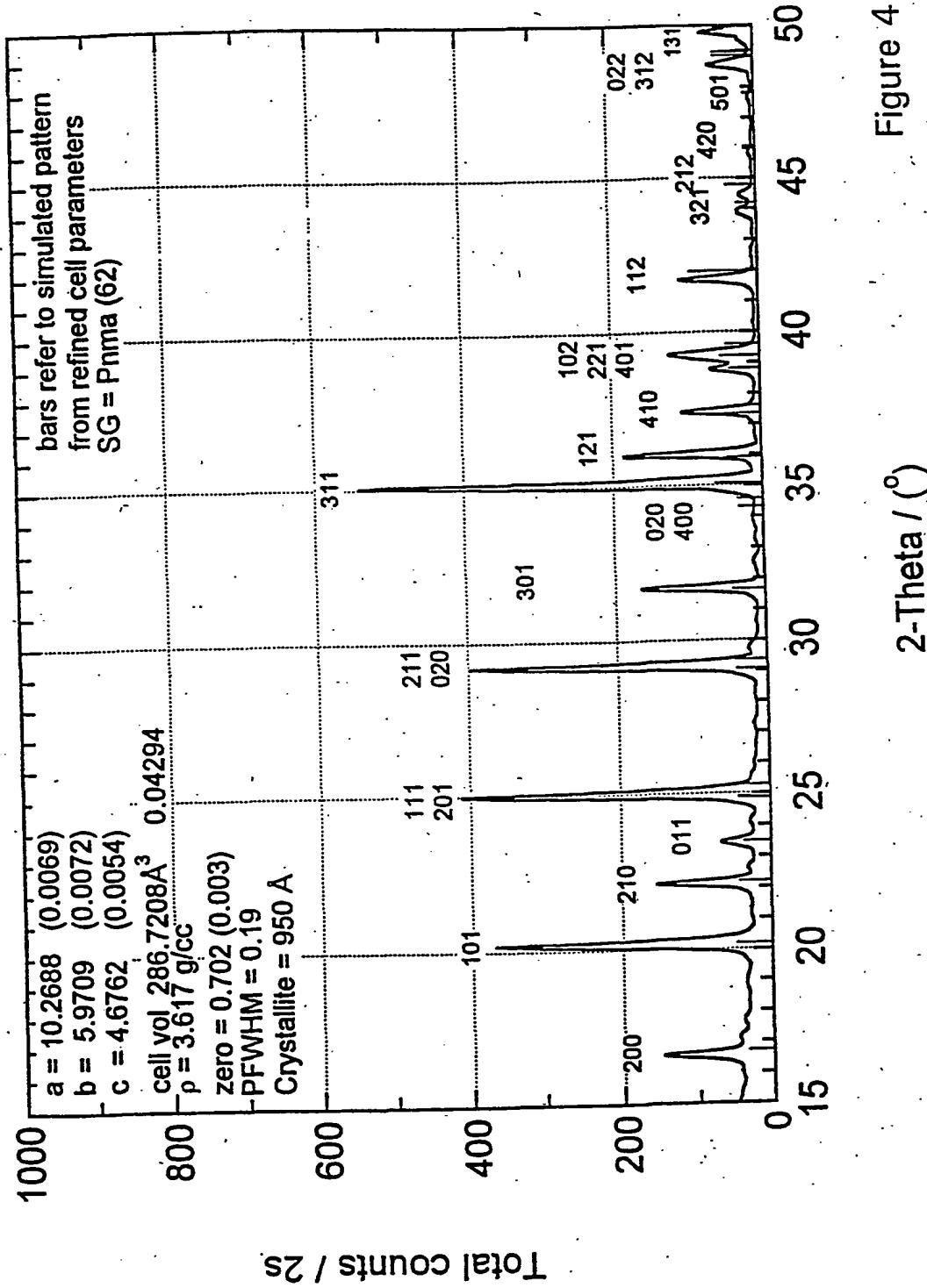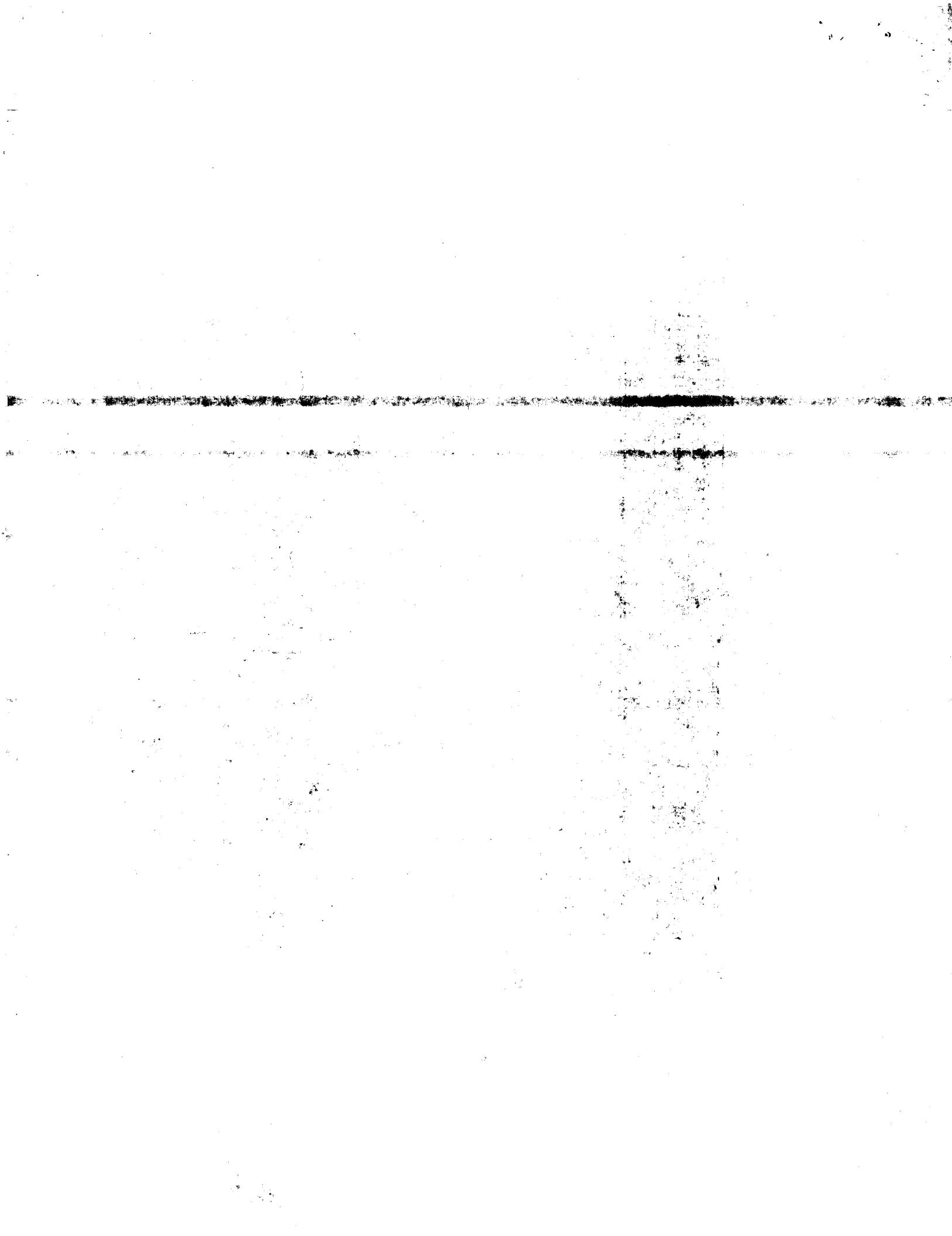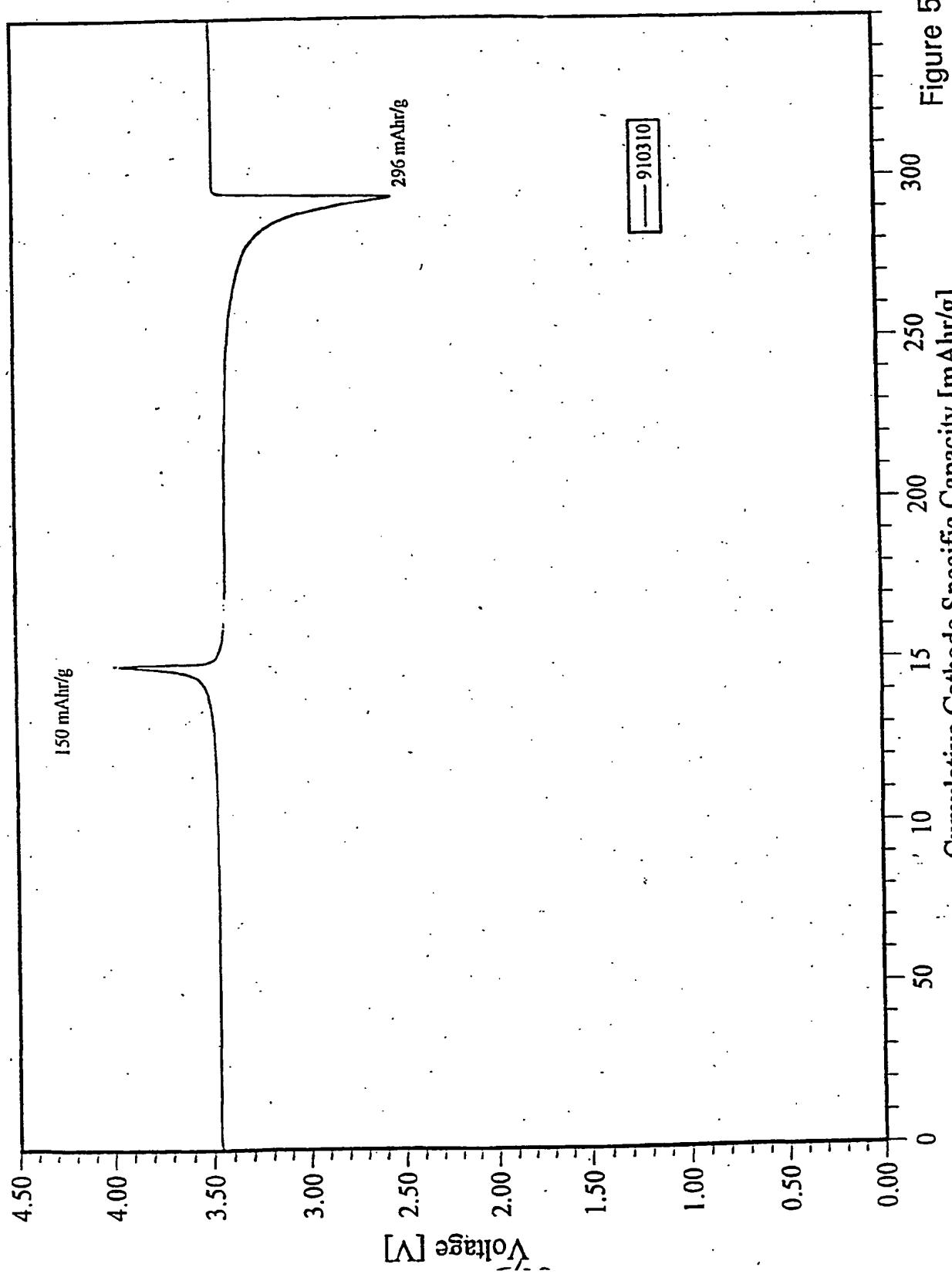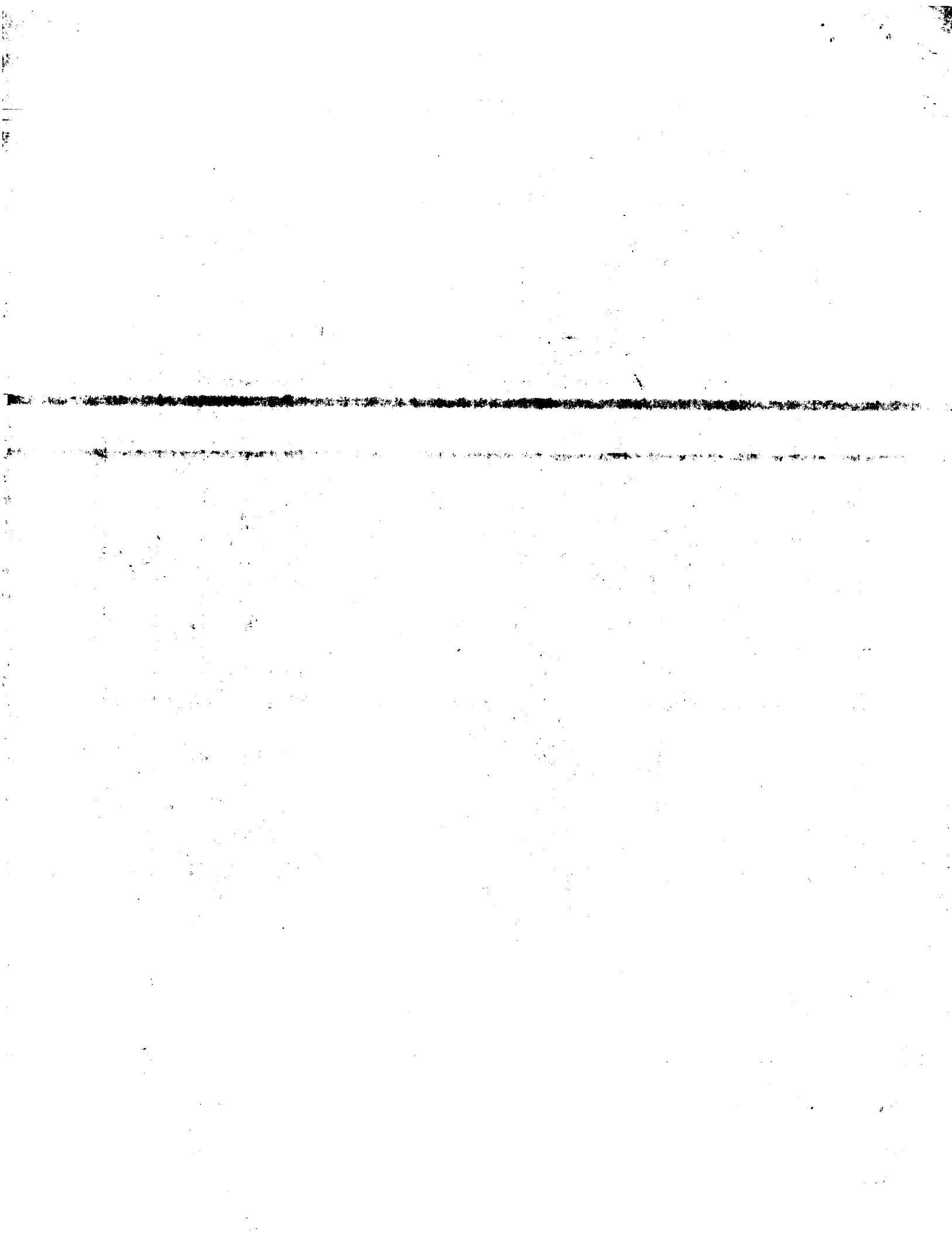
Figure 5

Carbothermal LiMg0.1Fe0.9PO4 vs Li
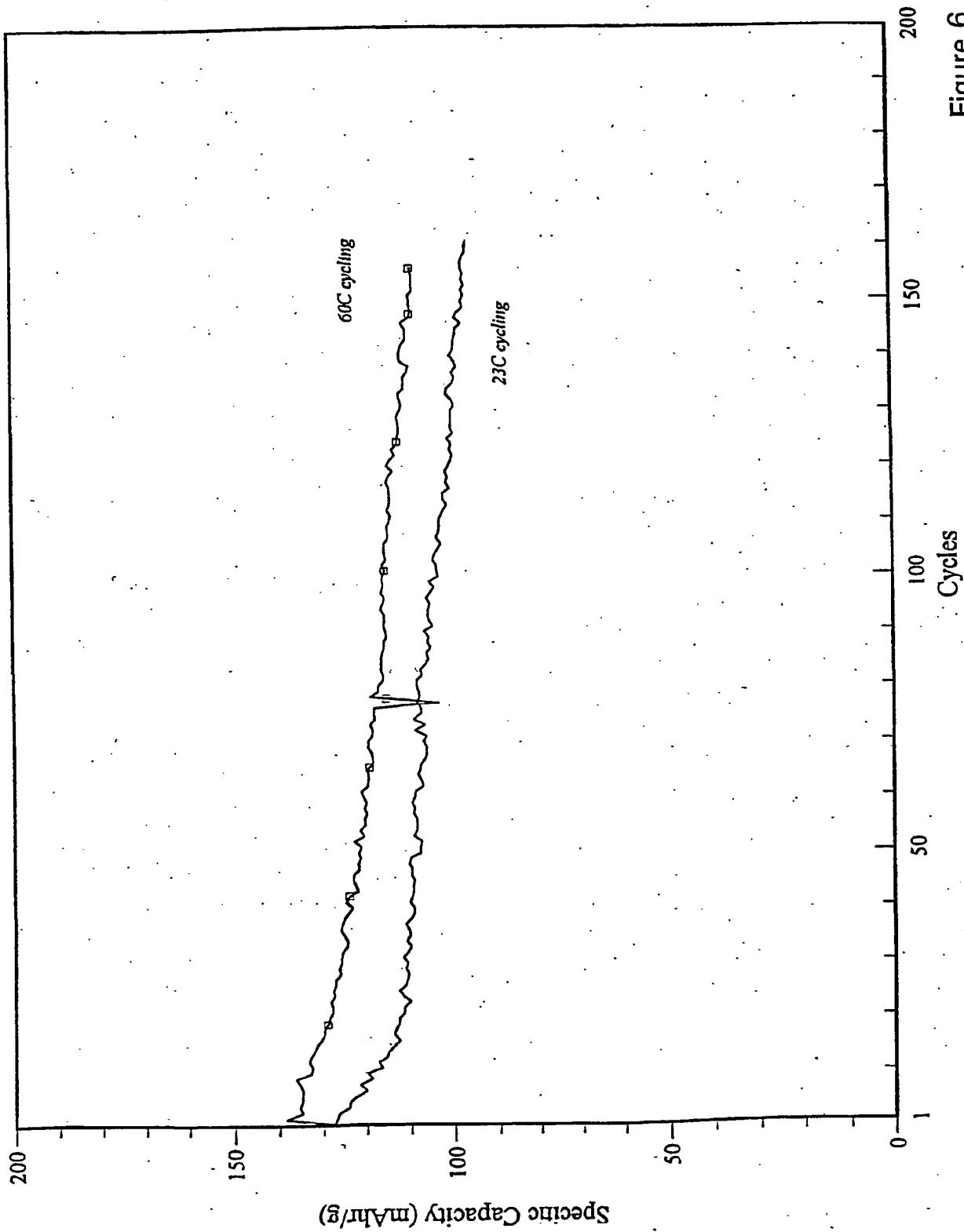
Figure 6
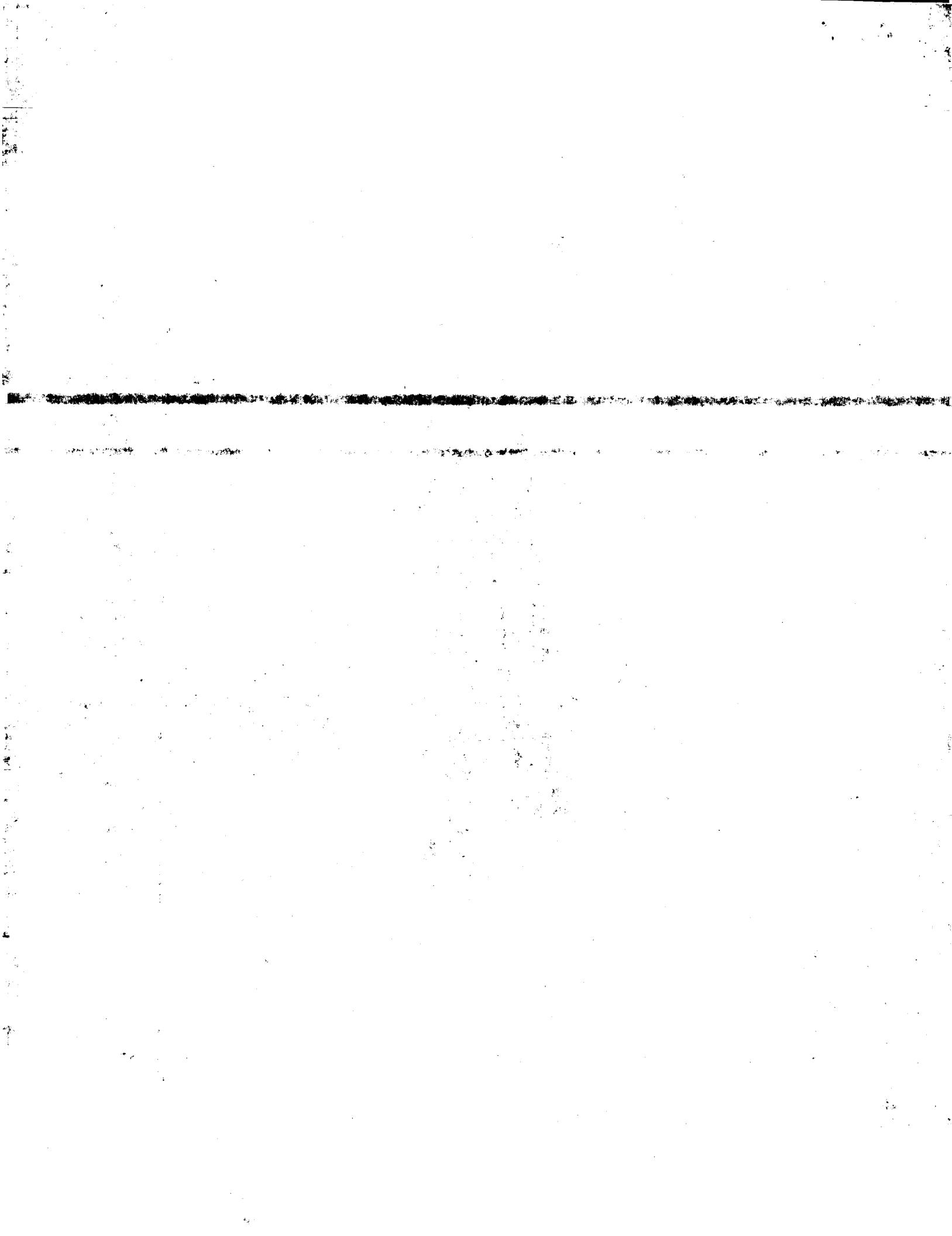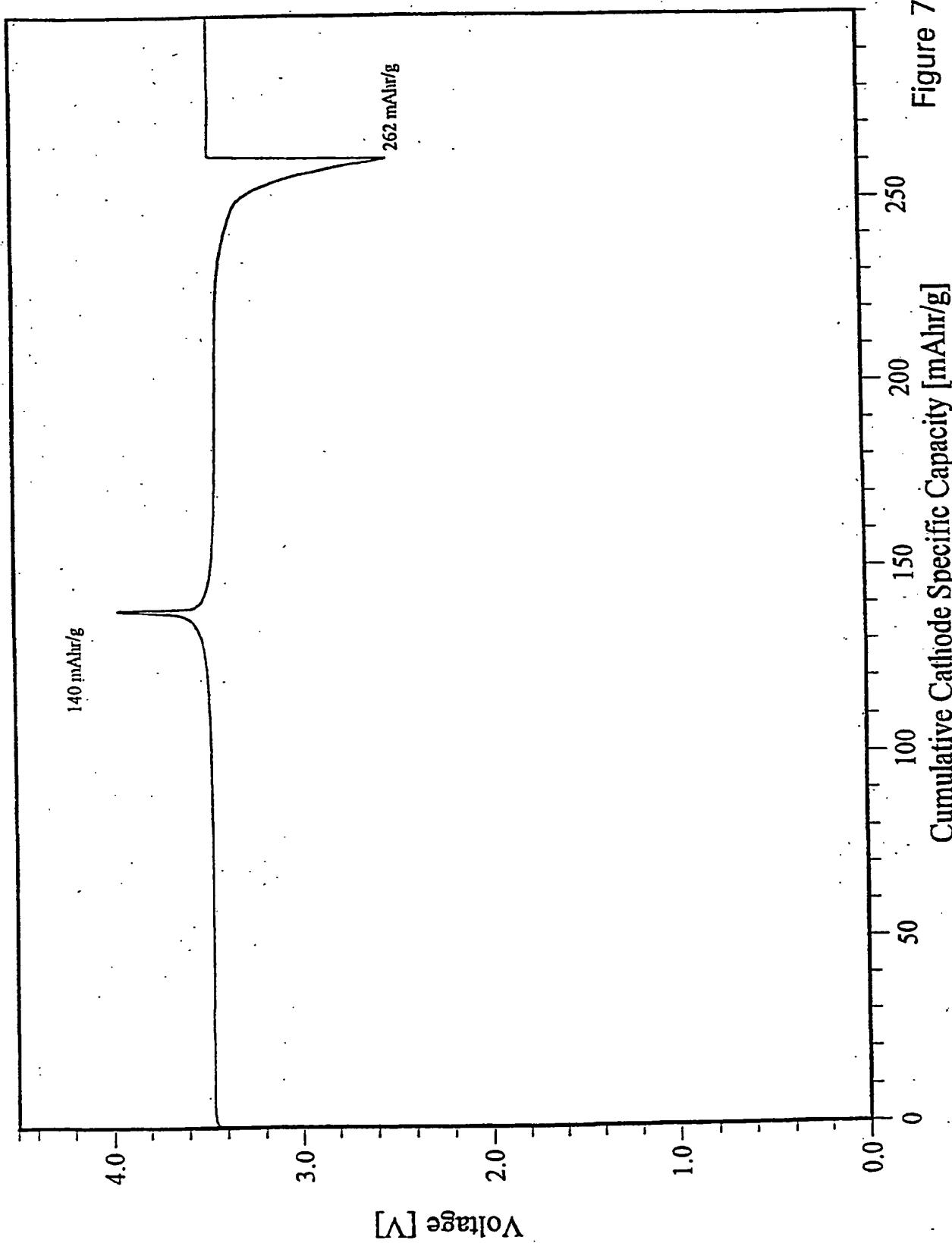
Figure 7

1S0937A1 (LiFe$_{0.9}$Ca$_{0.1}$PO$_4$)

a = 10.3240 (0.0045)
b = 6.0042 (0.0031)
c = 4.6887 (0.0020)
cell Volume = 290.6370Å$^3$ (0.1807)
zero = 0.702 (0.003)
ρ = 3.62 g/cc
PFWHM = 0.18
Crystallite = 680

bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)

Figure 8

LiFe0.8Ca0.2PO4  2.5 - 4.0 V

233 mAhr/g

123 mAhr/g

Voltage [V]

Cumulative Cathode Specific Capacity [mAhr/g]
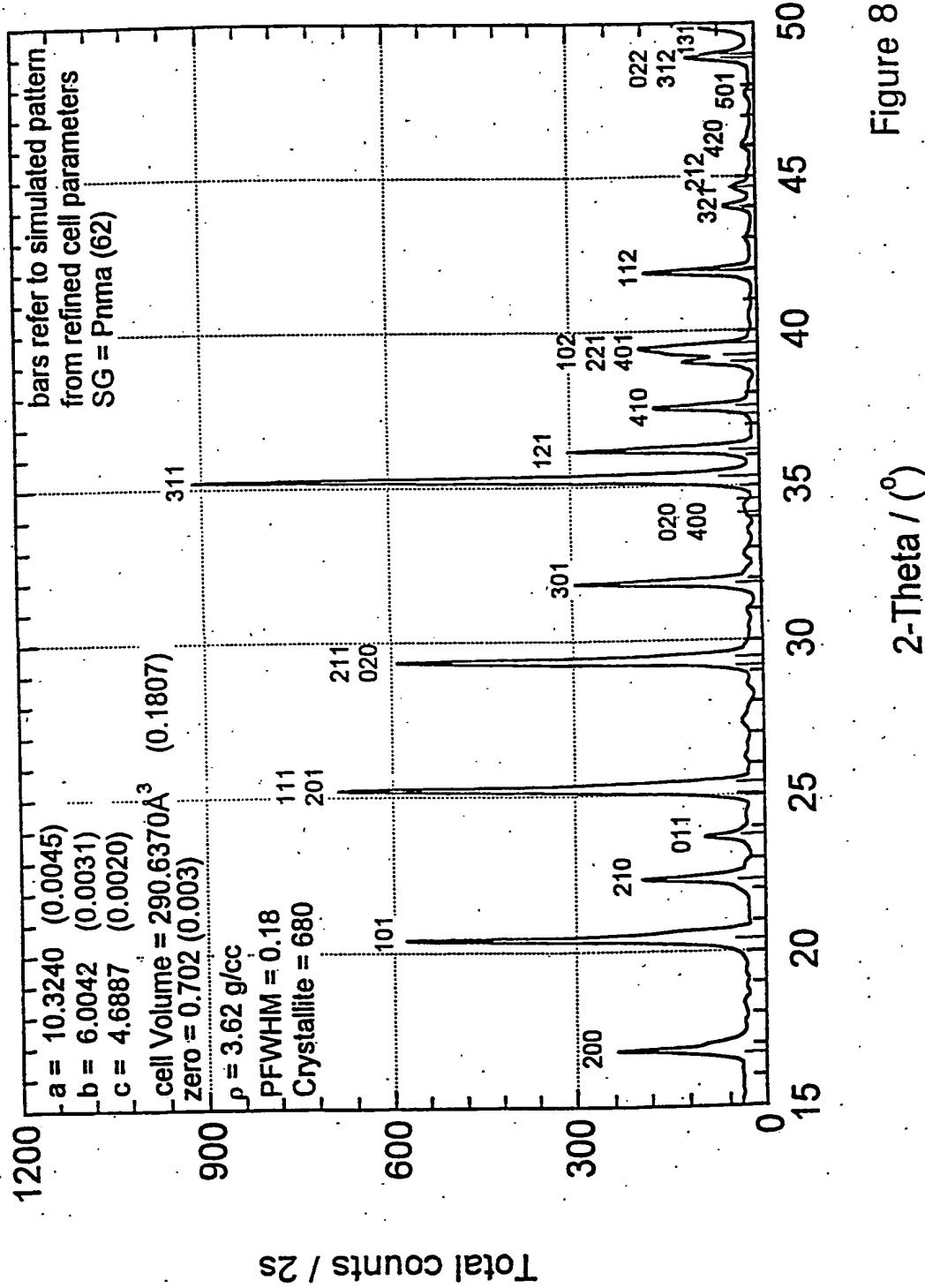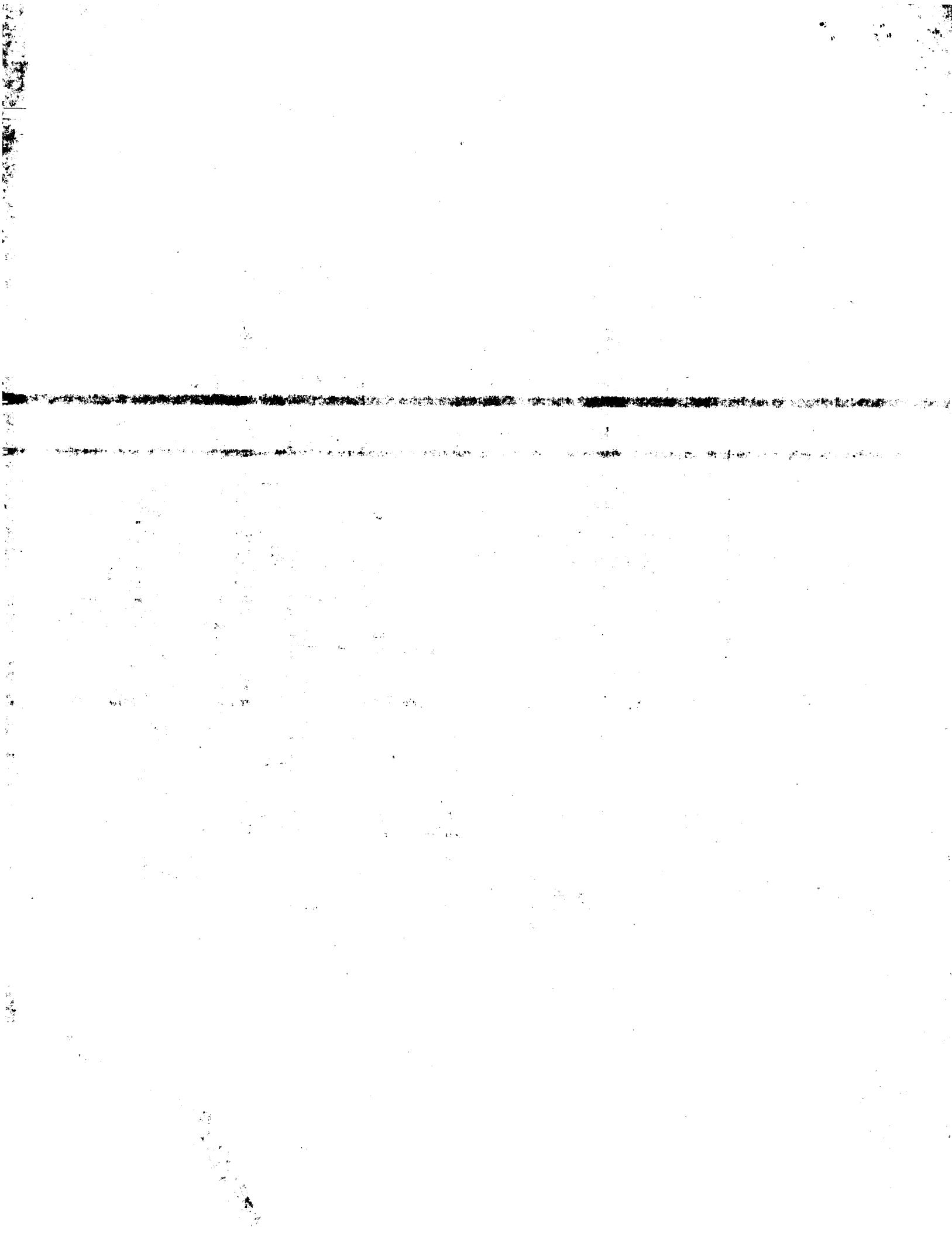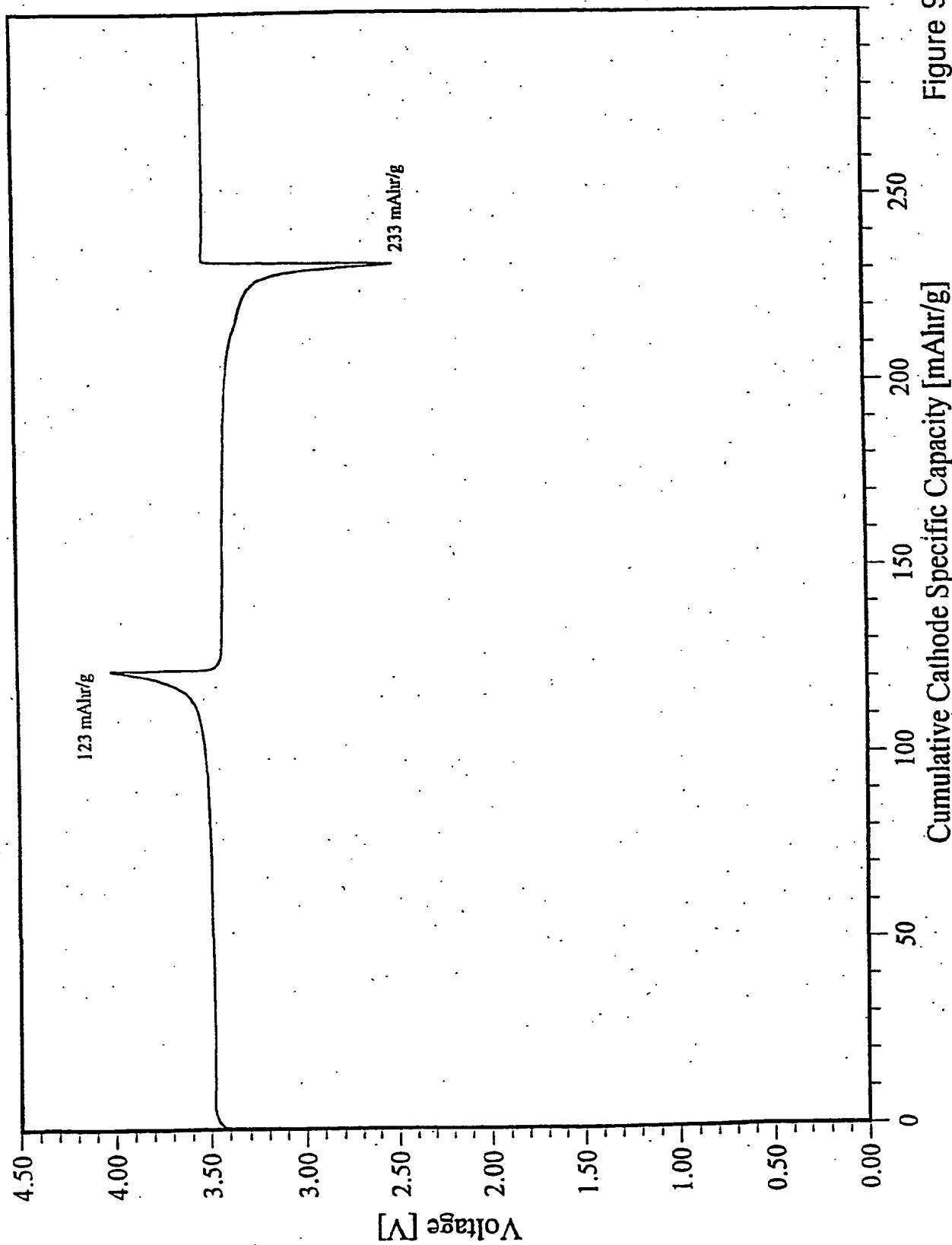
Figure 9

LiFe0.8Zn0.2PO4  2.5 - 4.0 V

124 mAhr/g

232 mAhr/g

Voltage [V]

Cumulative Cathode Specific Capacity [mAhr/g]
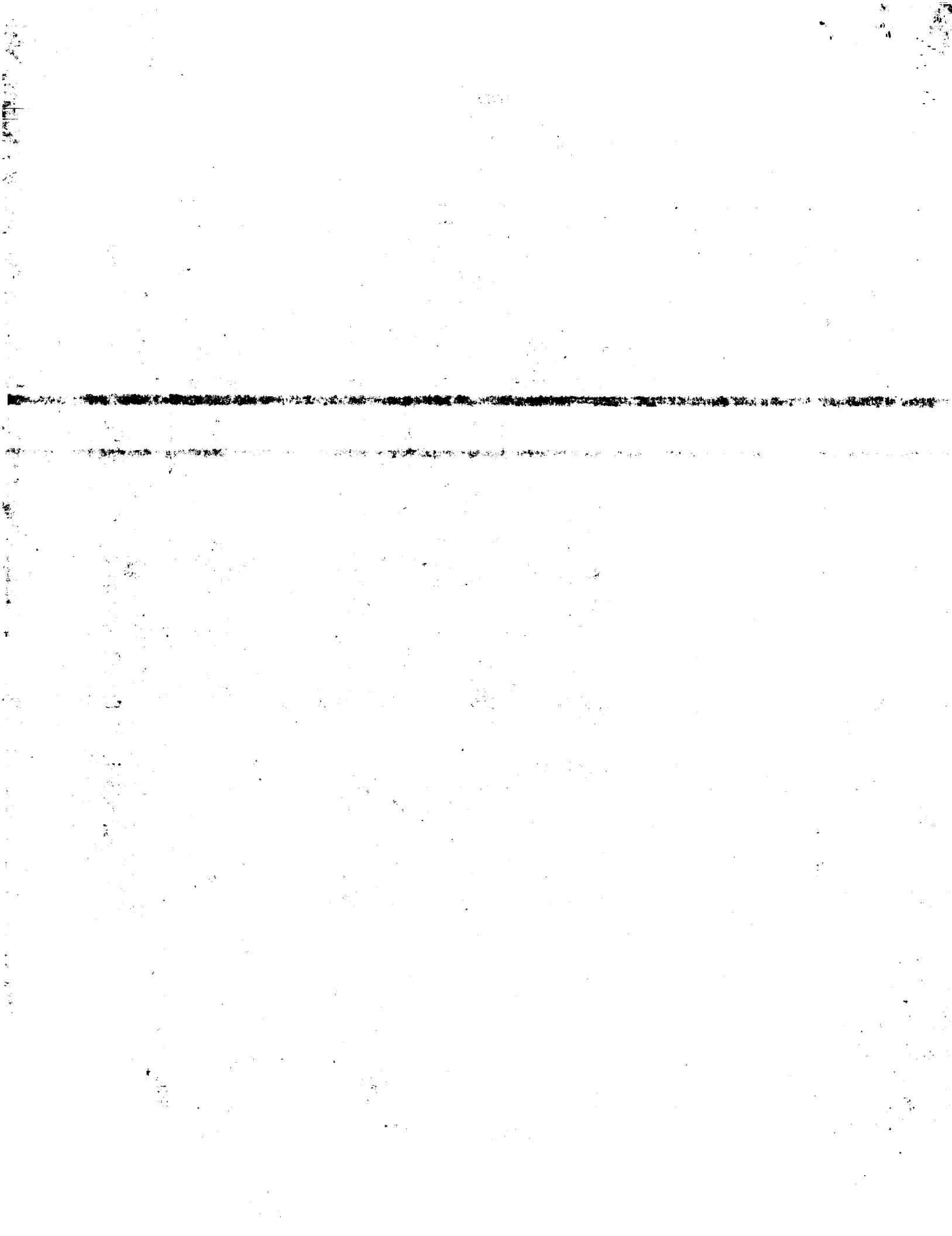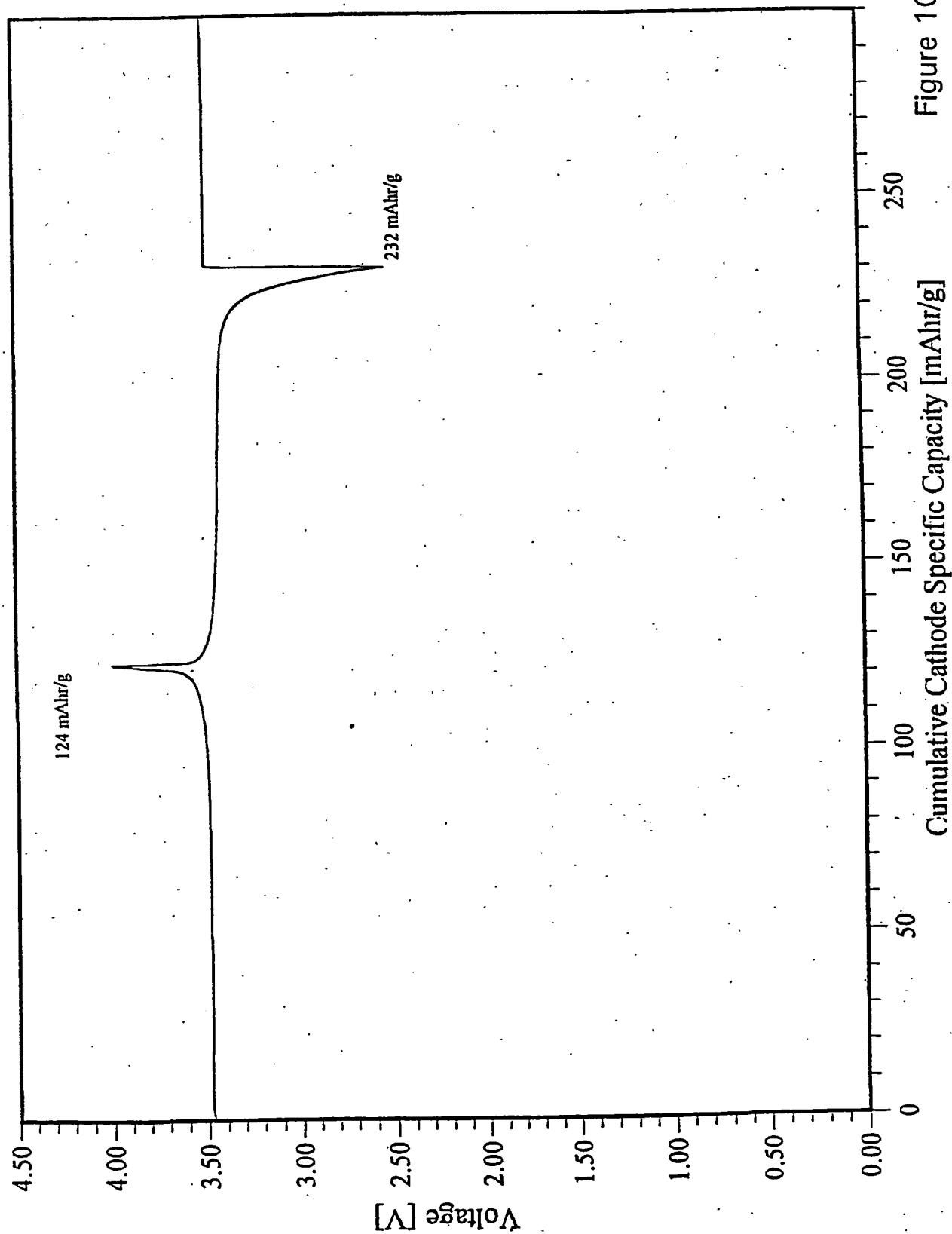
Figure 10

gamma- $Li_xV_2O_5$ - carbo-thermal

CuKα (1.5405A°)
Phase type : γ-$Li_xV_2O_5$ (x=1)
Symmetry : Orthorhombic.
Space Group :Pnma
a = 9.687 (1)
b = 3.603 (2)
c=10.677 (3)

Figure 11

2-theta (°)

Intensity (cps)
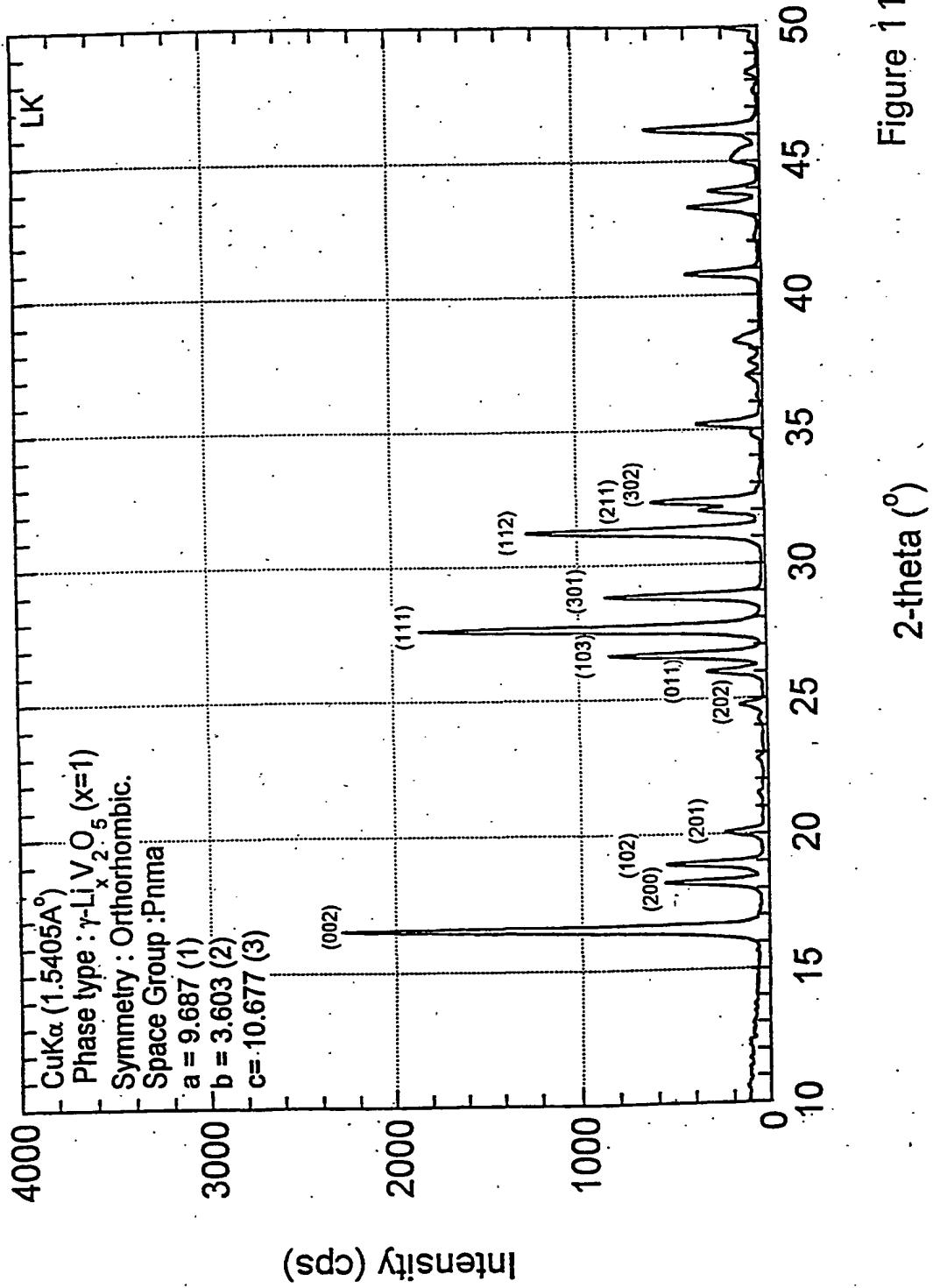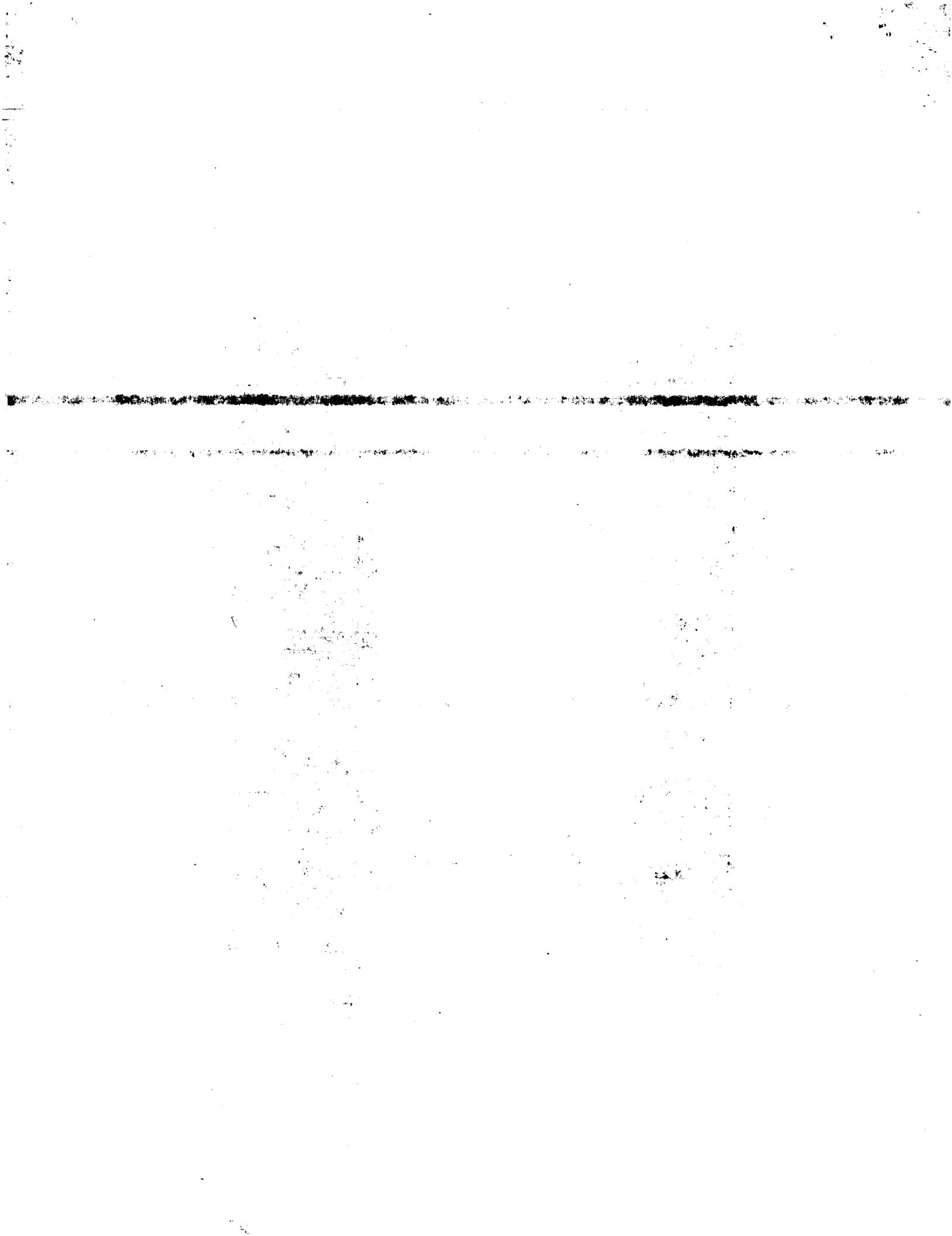
gamma- LiV2O5 Synthesized by Carbothermal Reduction Method
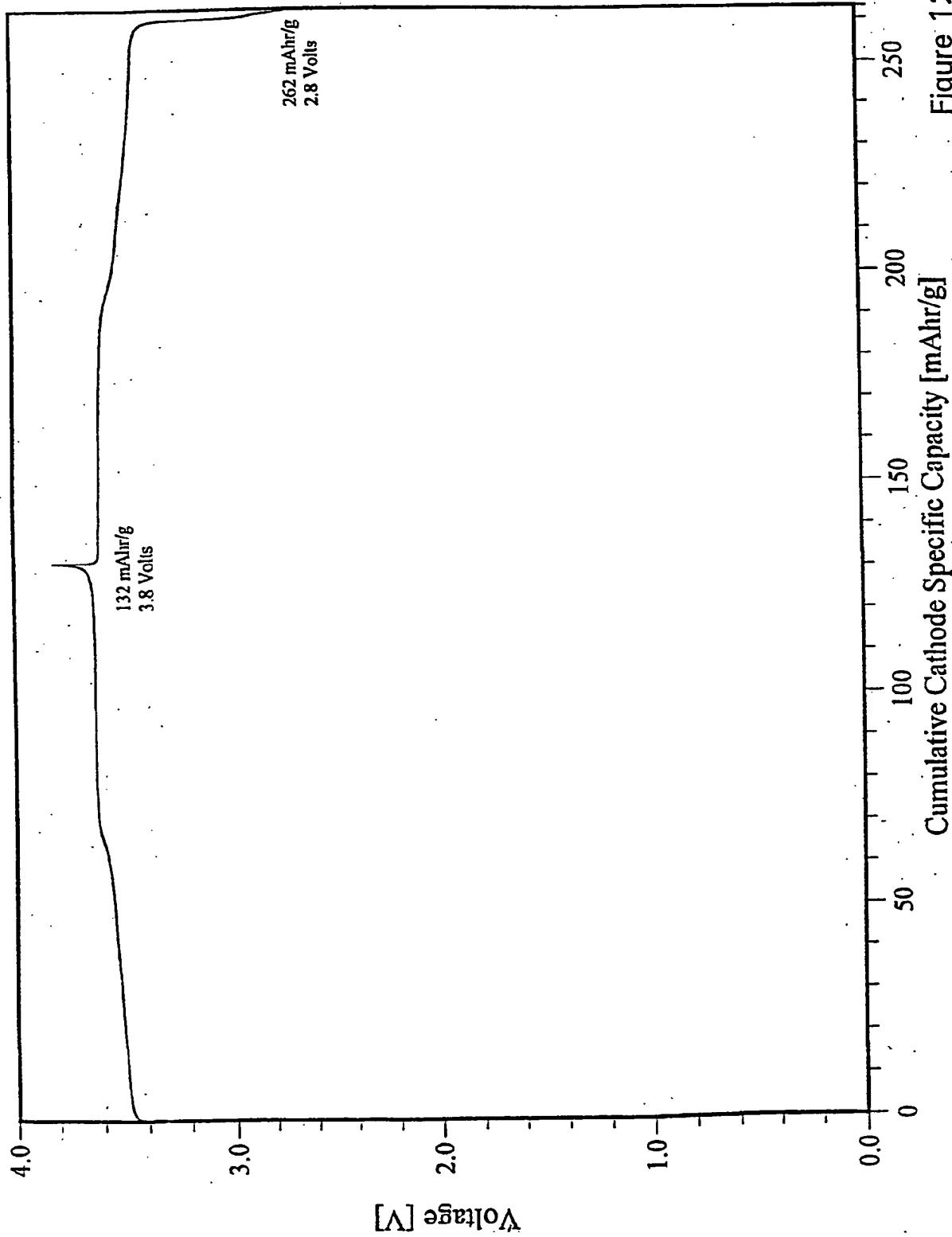
Figure 12
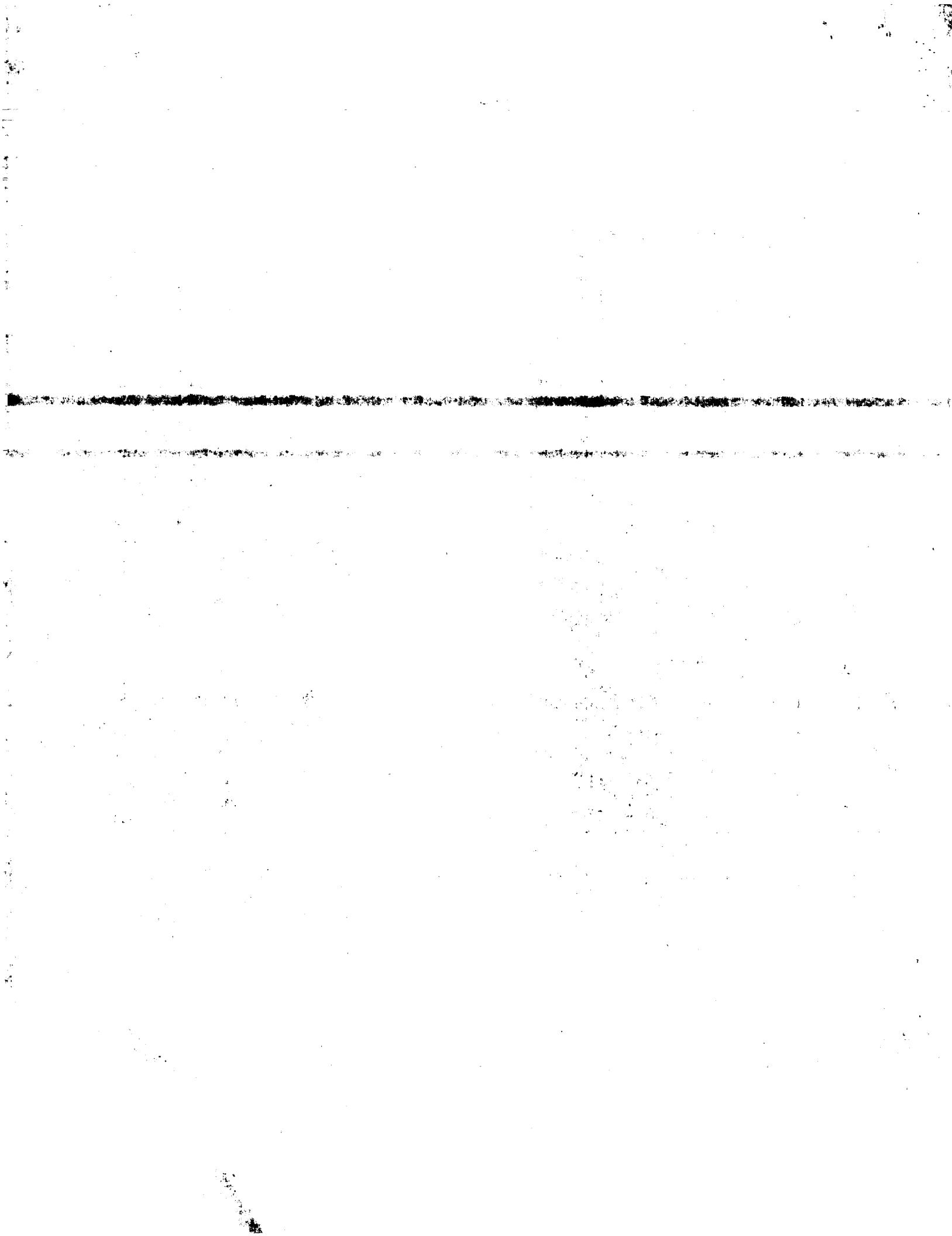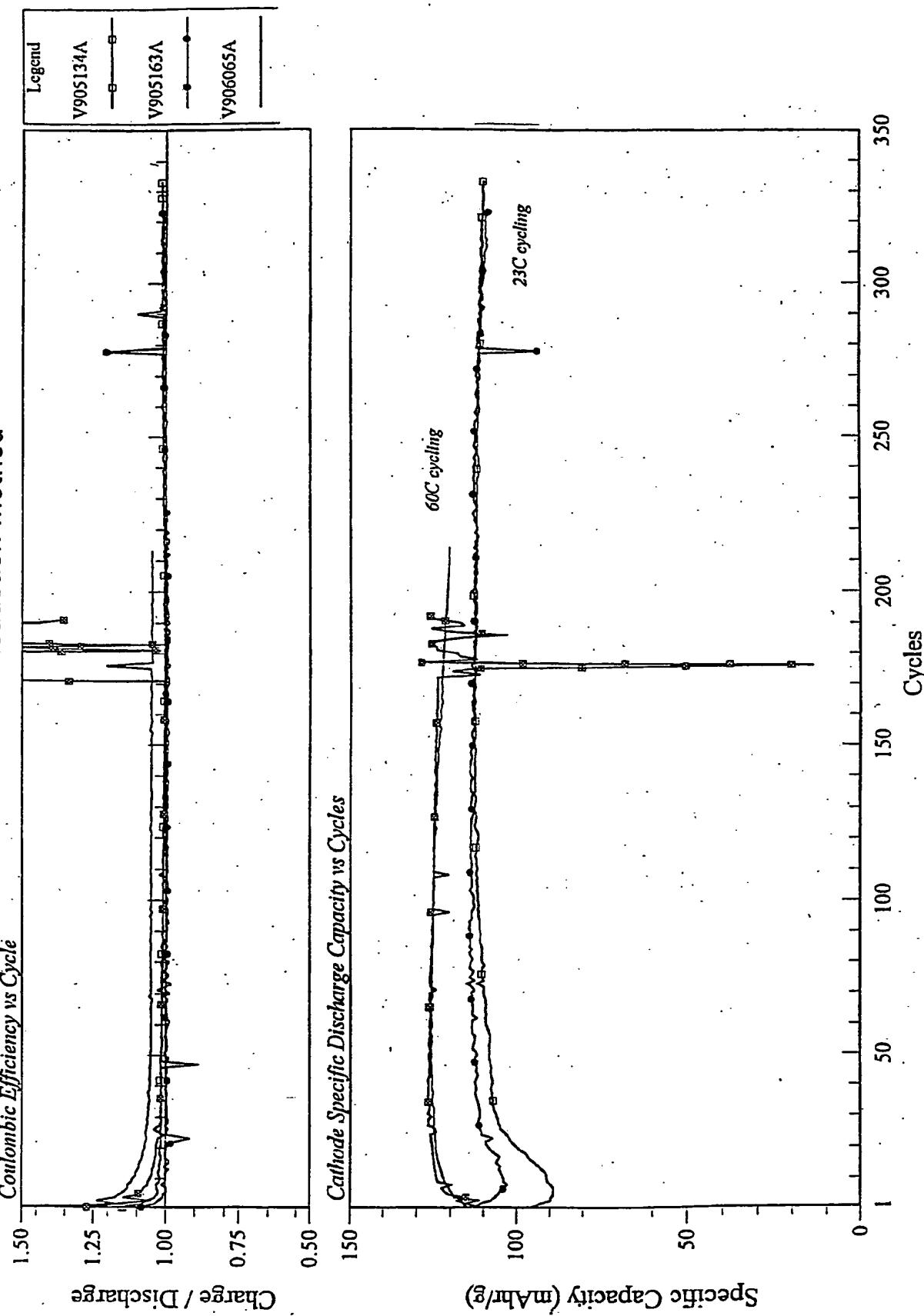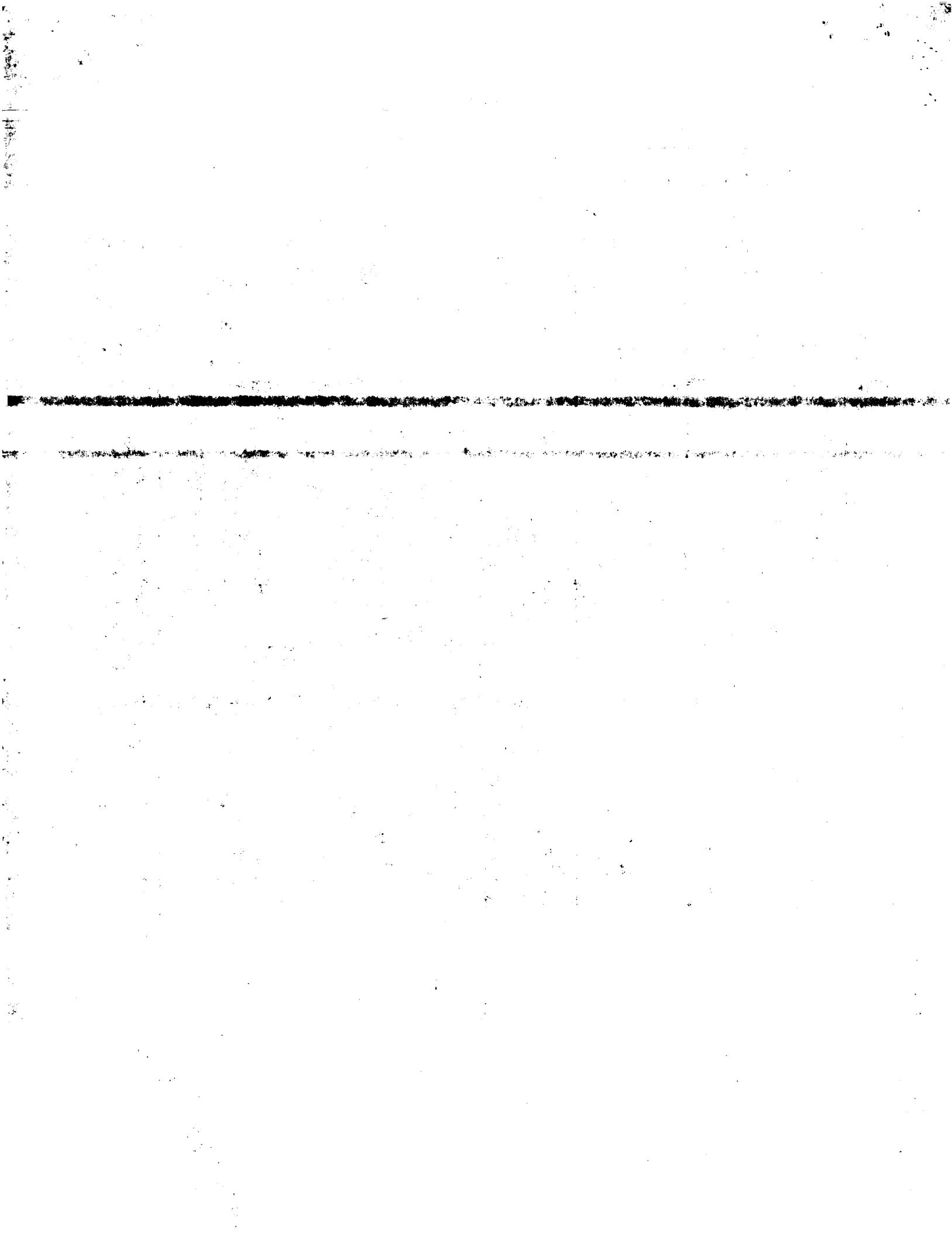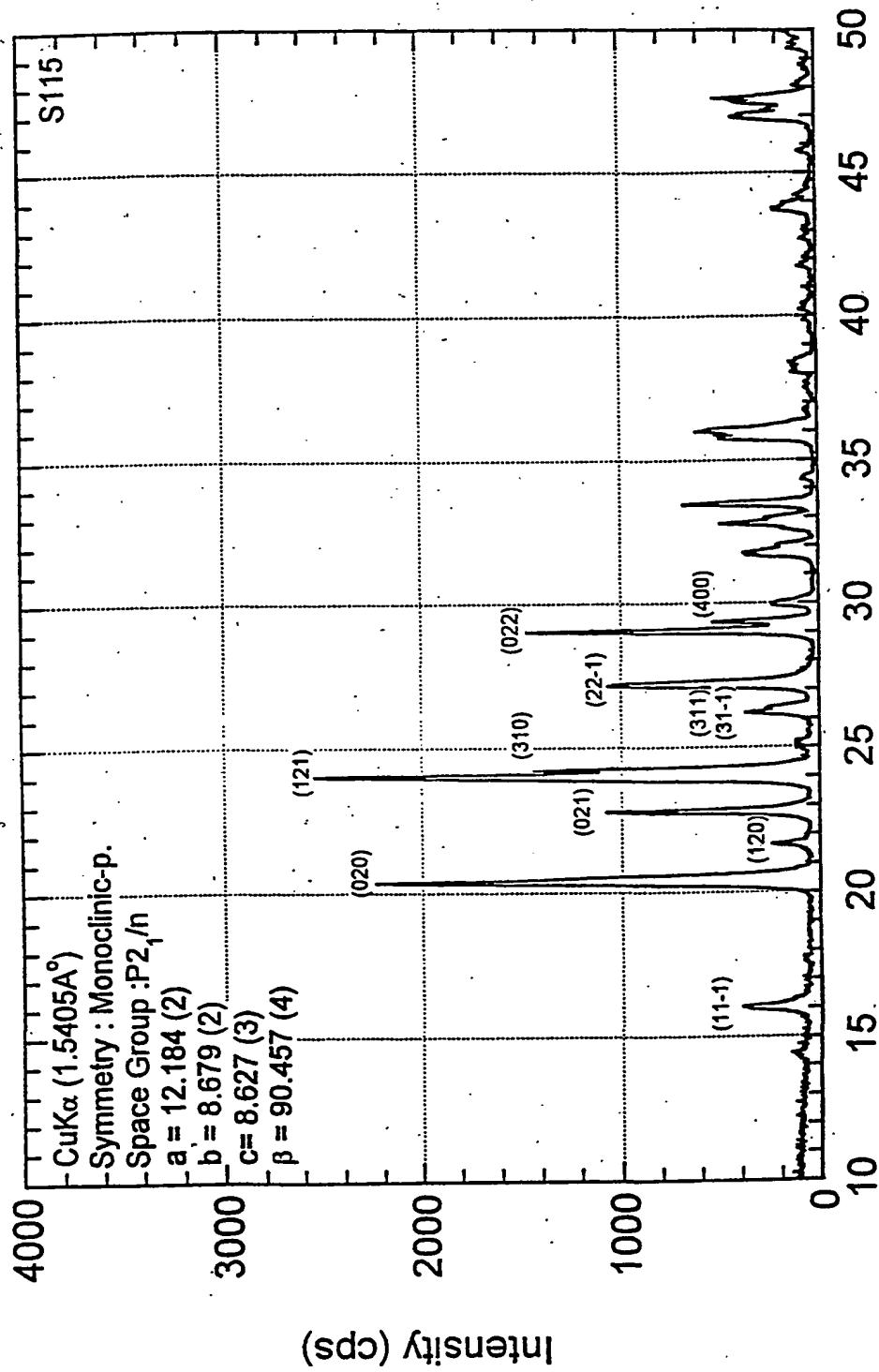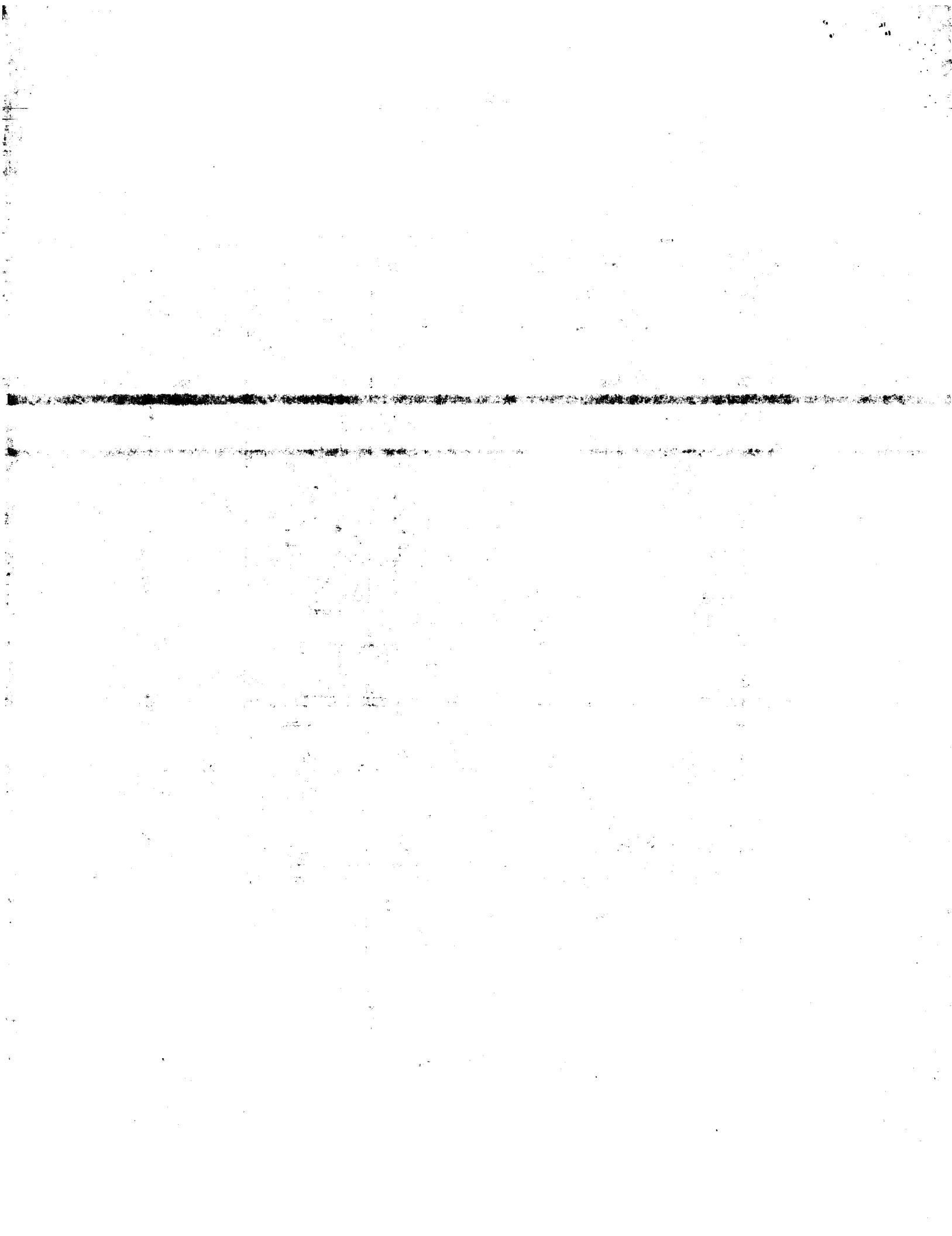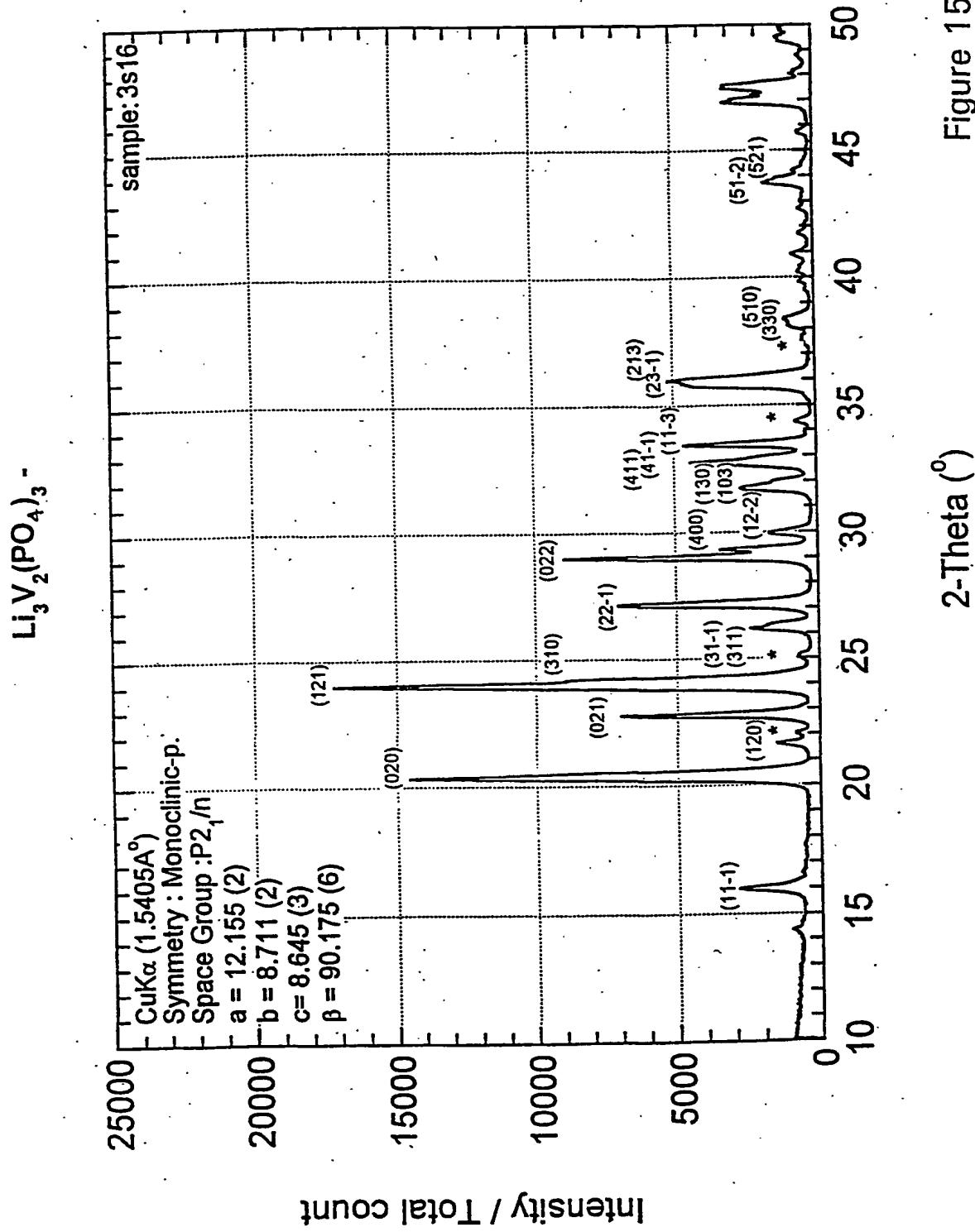
Figure 13
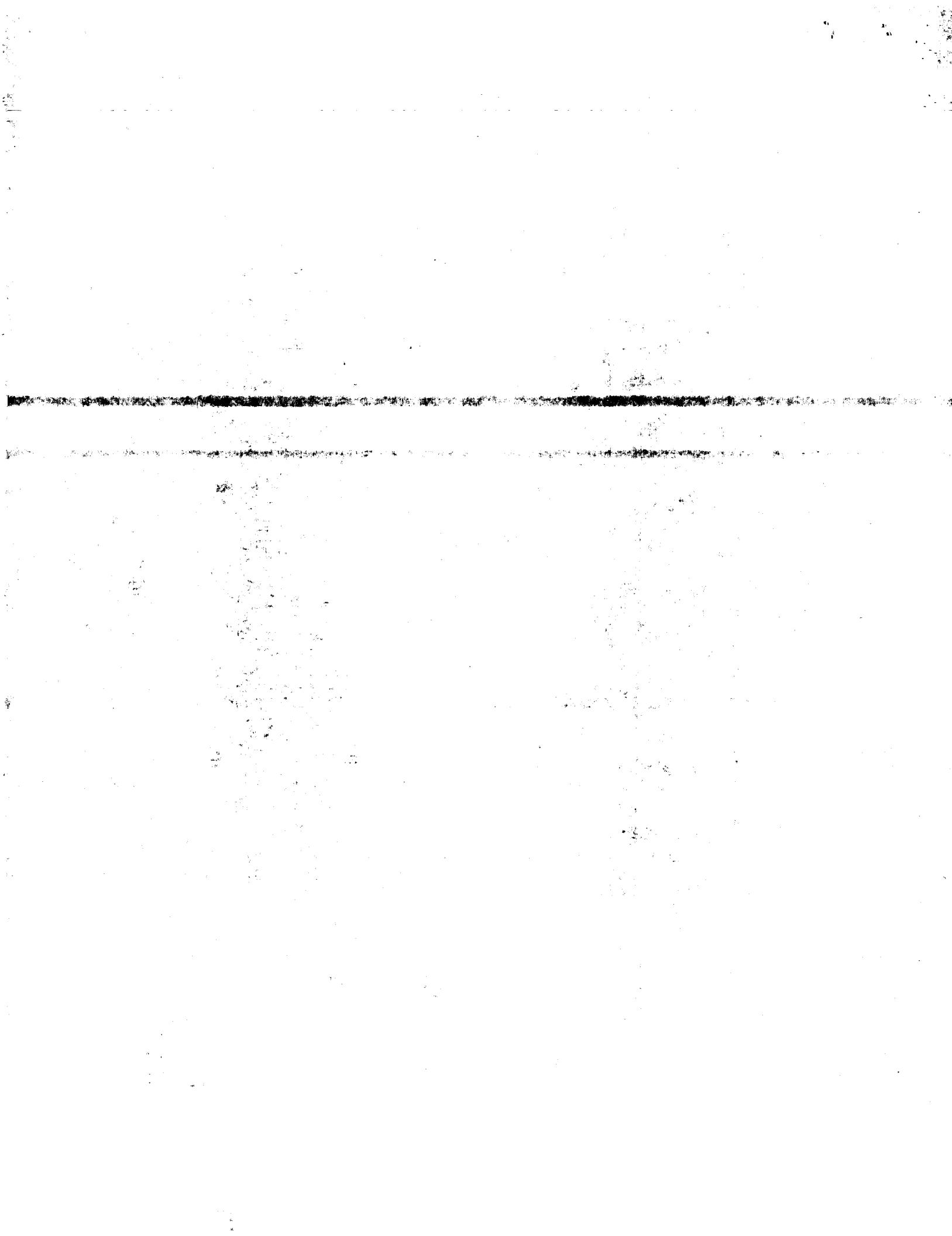
Figure 14

Figure 15

Li3V2(PO4)3  Synthesis by Carbothermal Reduction Method  13.8 mg active

133 mAhr/g
4.19 Volts

4 mAhr/g
2.97 Volts

Voltage [V]

Cathode Specific Capacity [mAhr/g]
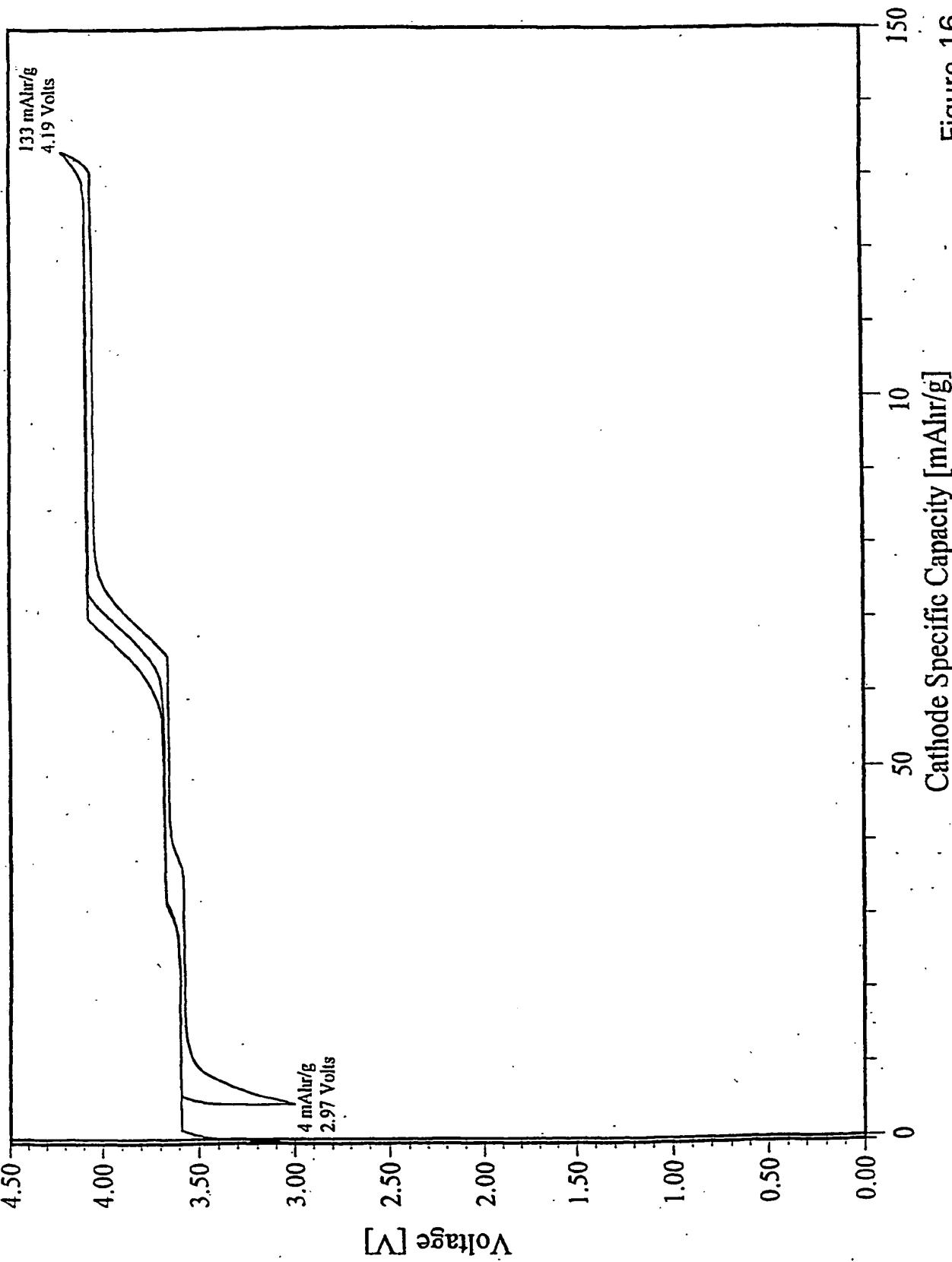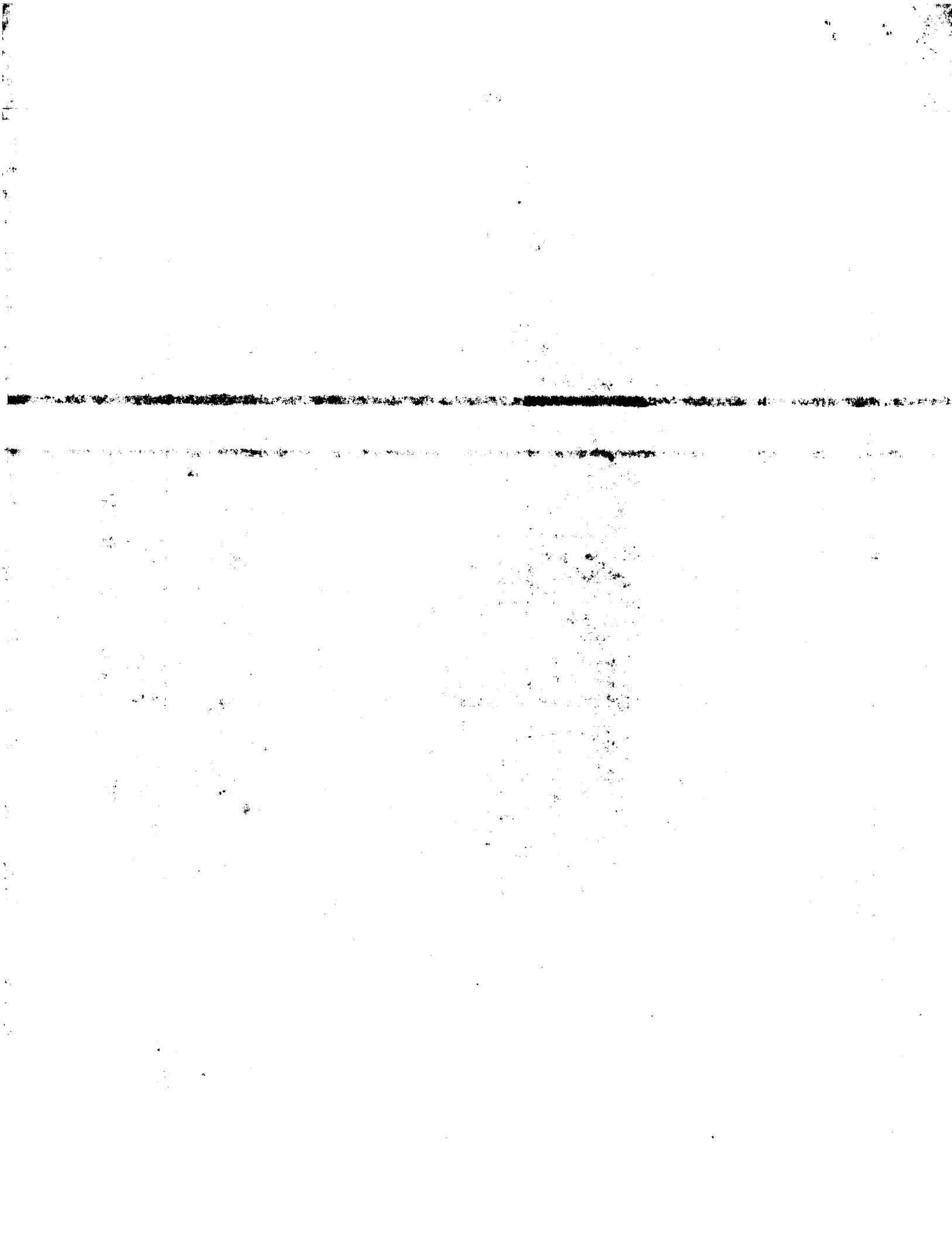
Figure 16

Li3V2(PO4)3 Synthesis by Carbothermal Reduction Method
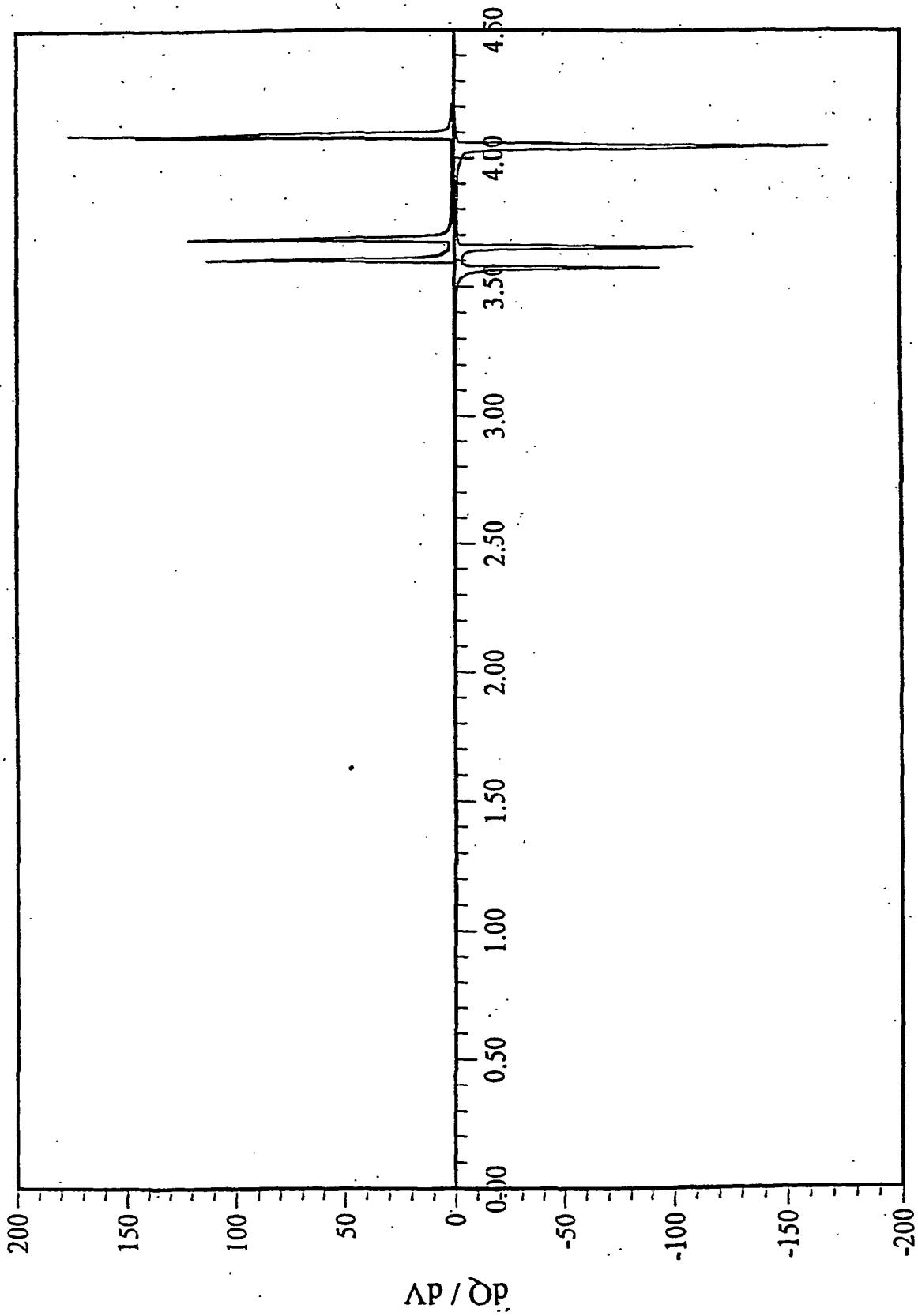
Figure 17
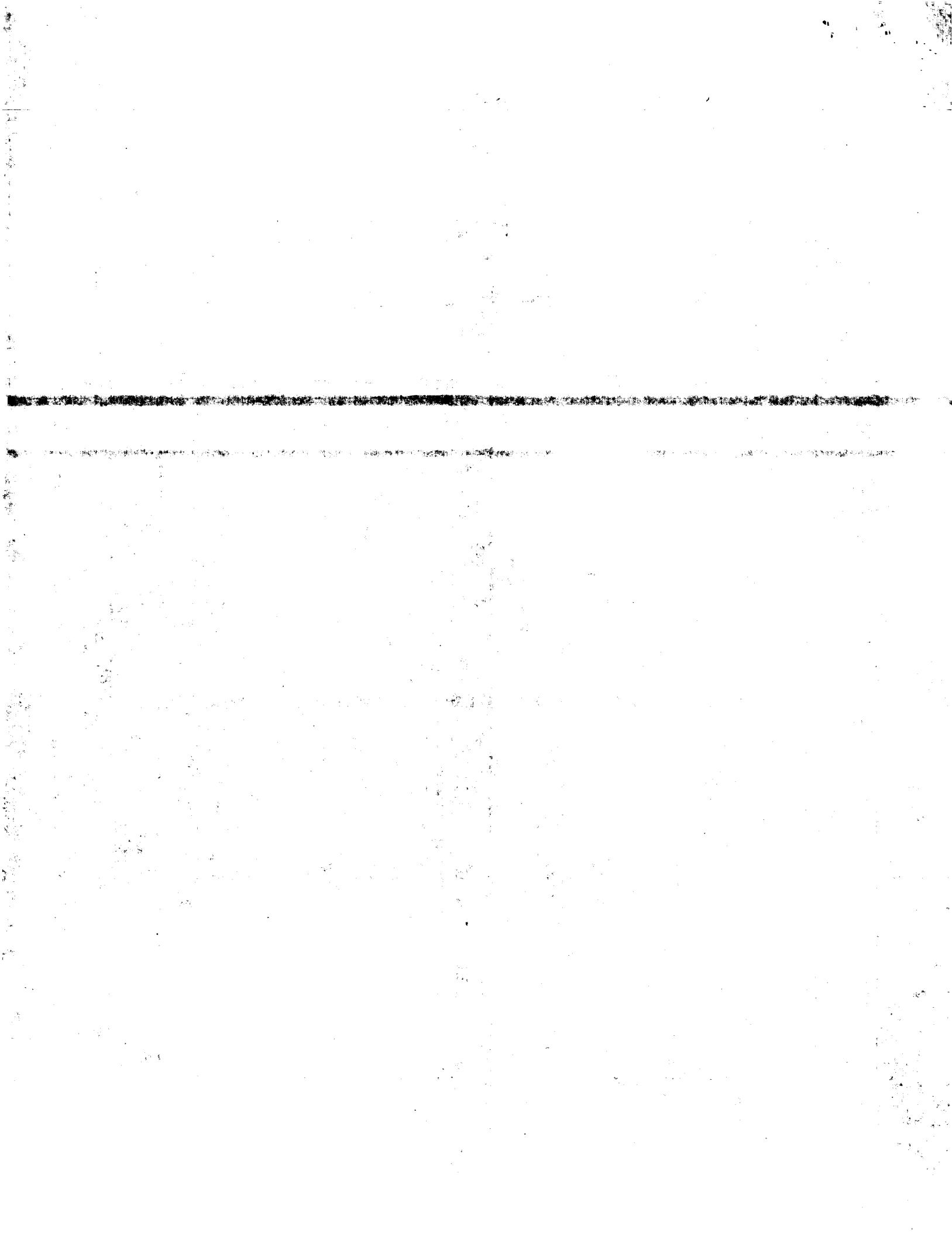
Voltage [V]

Carbothermal LiMg0.2Fe0.8PO4 vs Li

60C Cycling

23C Cycling

Specific Capacity (mAhr/g)

Cycles
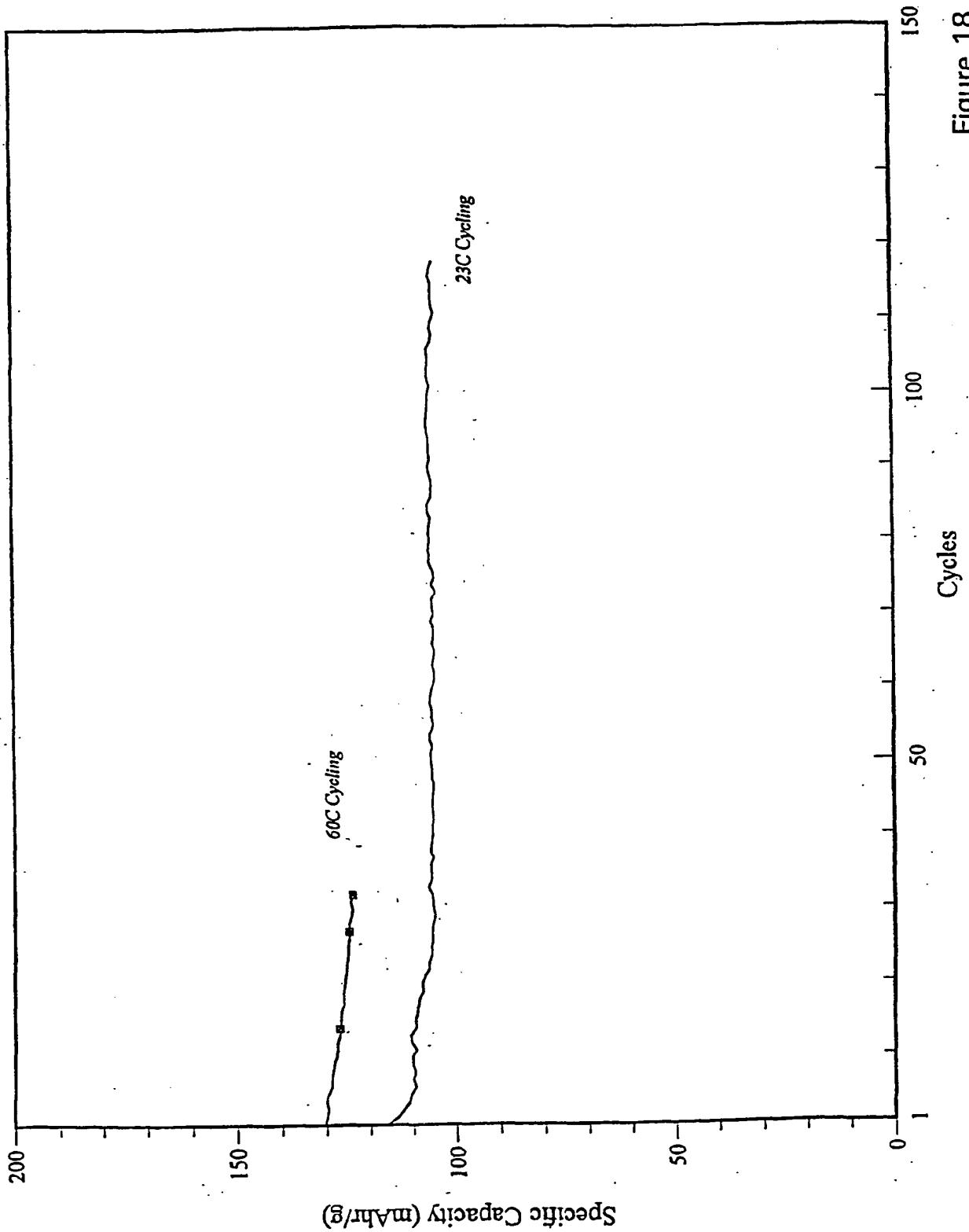
Figure 18

Voltage Profile for LiMg0.1Fe0.9PO4 vs MCMB
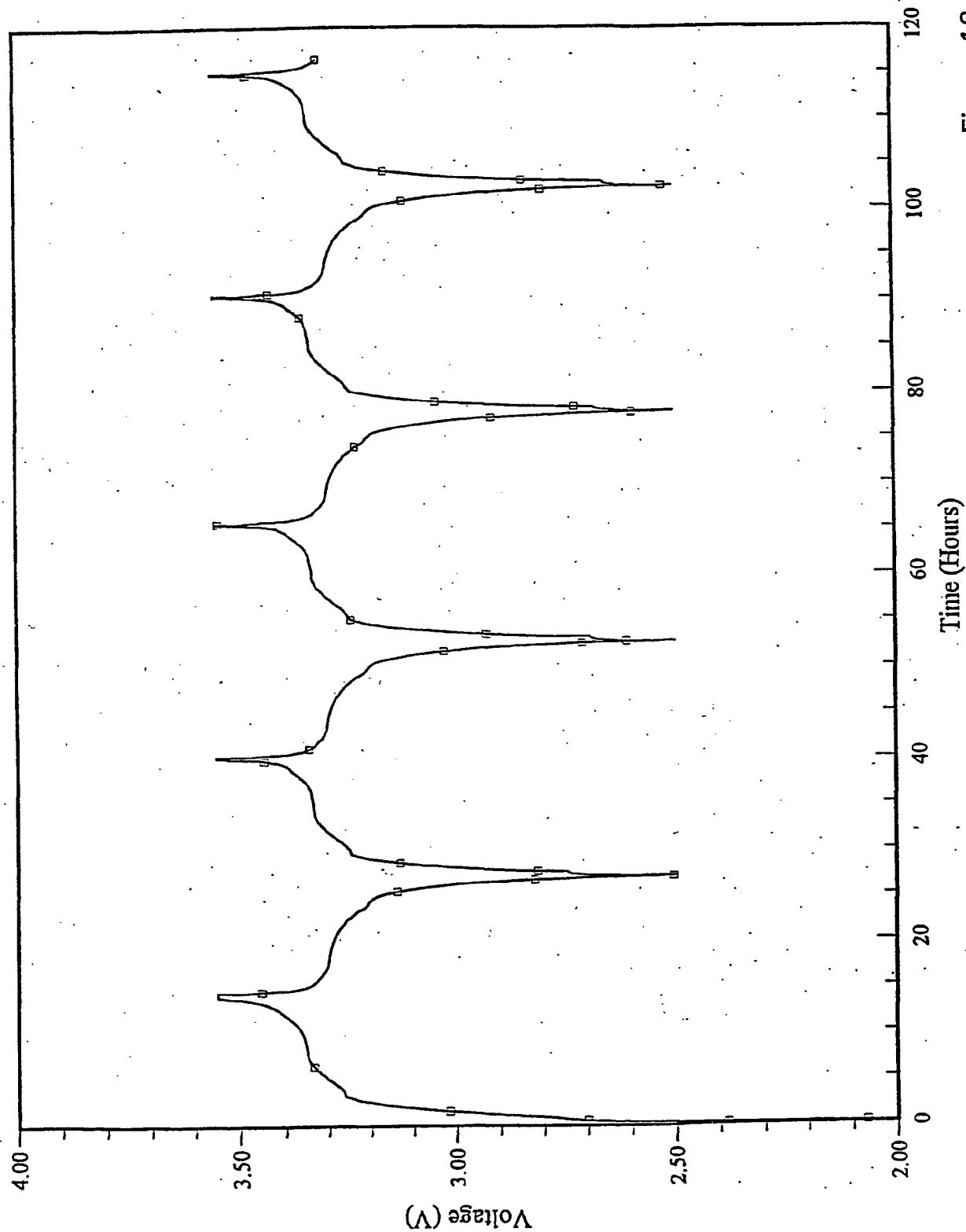


Figure 19

Carbothermal LiMg0.1Fe0.9PO4 vs MCMB

Coulombic Efficiency vs Cycle

Cathode Specific Discharge Capacity vs Cycles
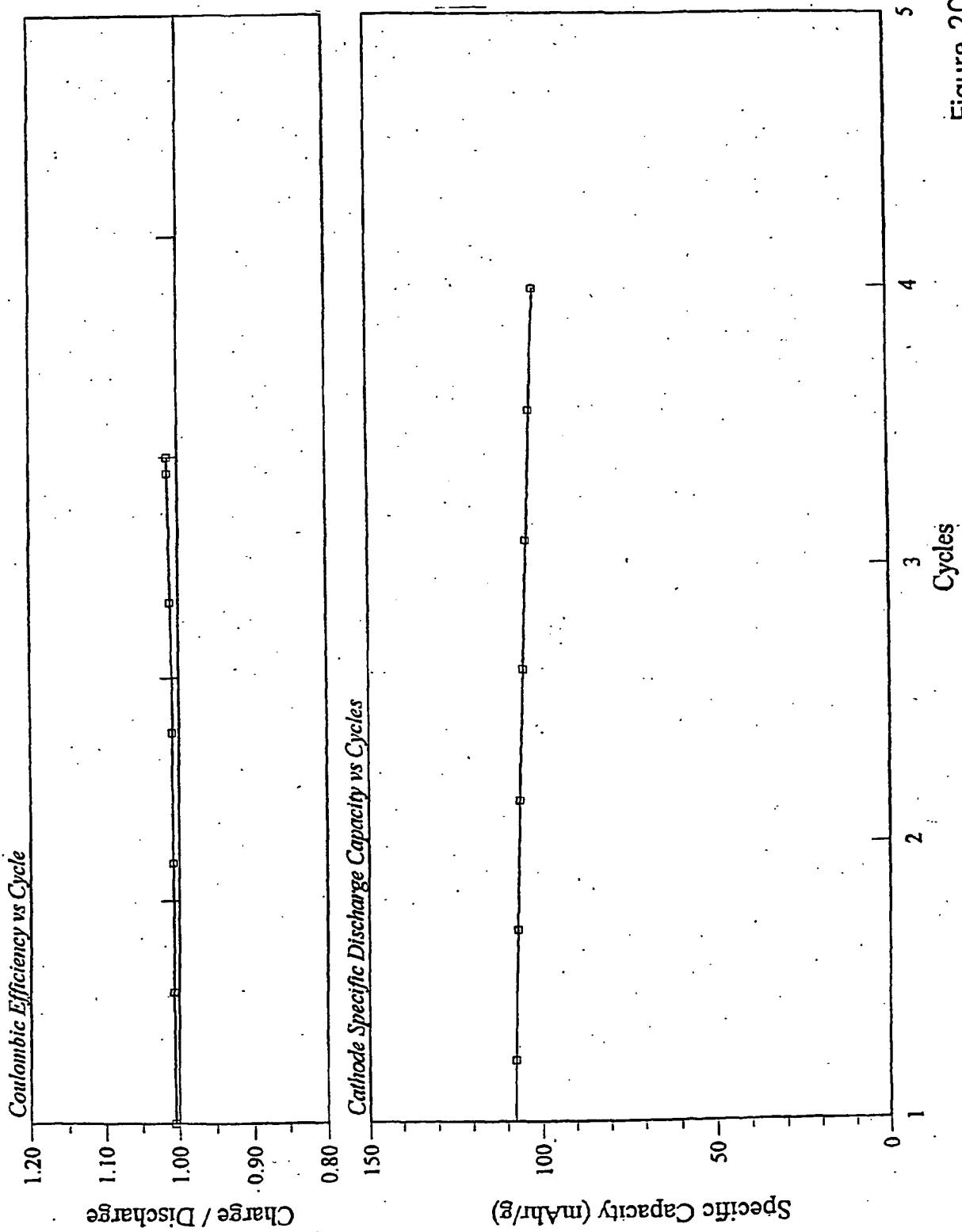
Figure 20

Figure 21

Carbothermal LiV2O5/MCMB2528  2.5-3.65 V
gamma-LiV$_2$O$_5$

129 mAhr/g
3.65 Volts

352 mAhr/g
3.65 Volts

569 mAhr/g
3.65 Volts

238 mAhr/g
2.47 Volts

457 mAhr/g
2.47 Volts

Cumulative Cathode Specific Capacity [mAhr/g]

Voltage [V]
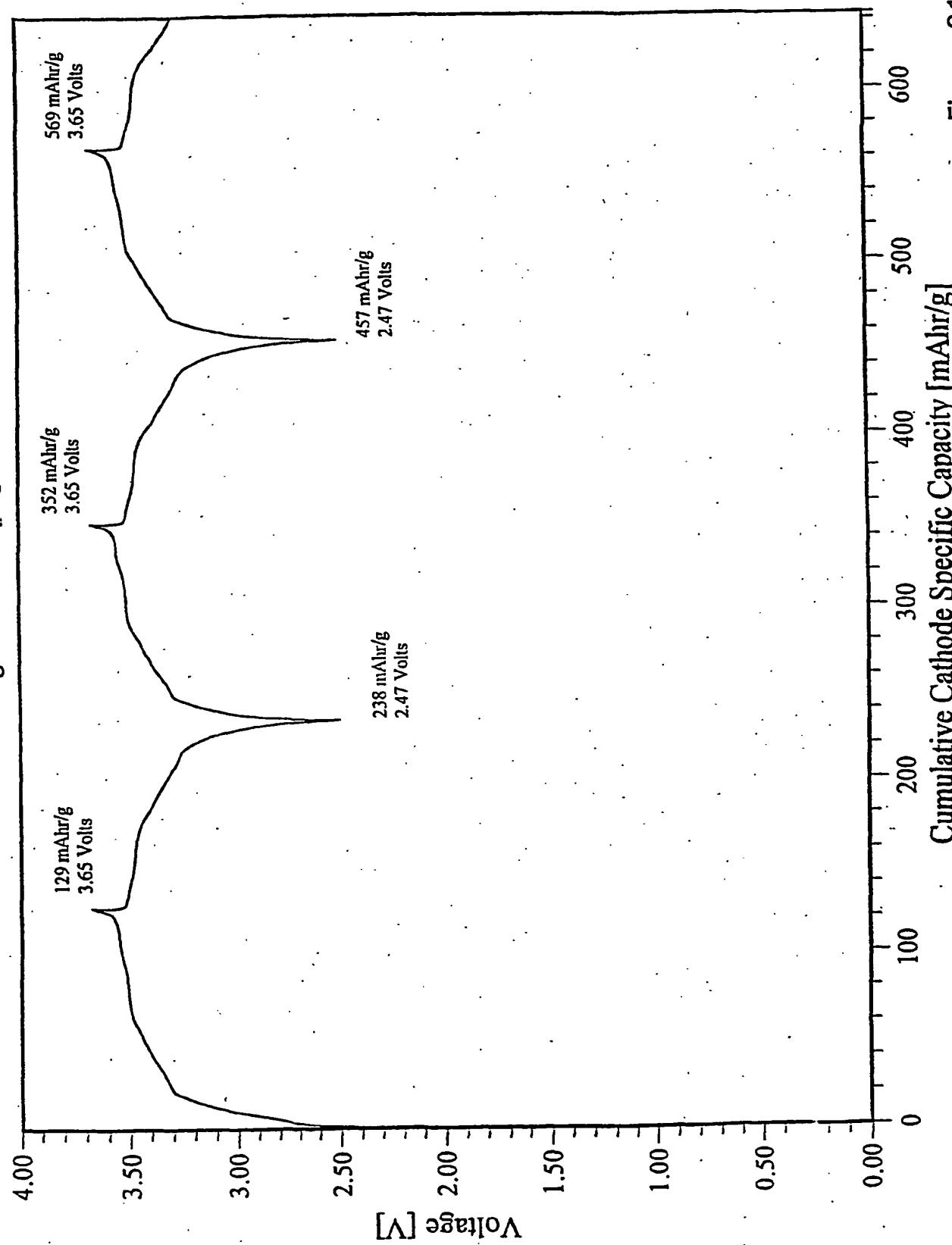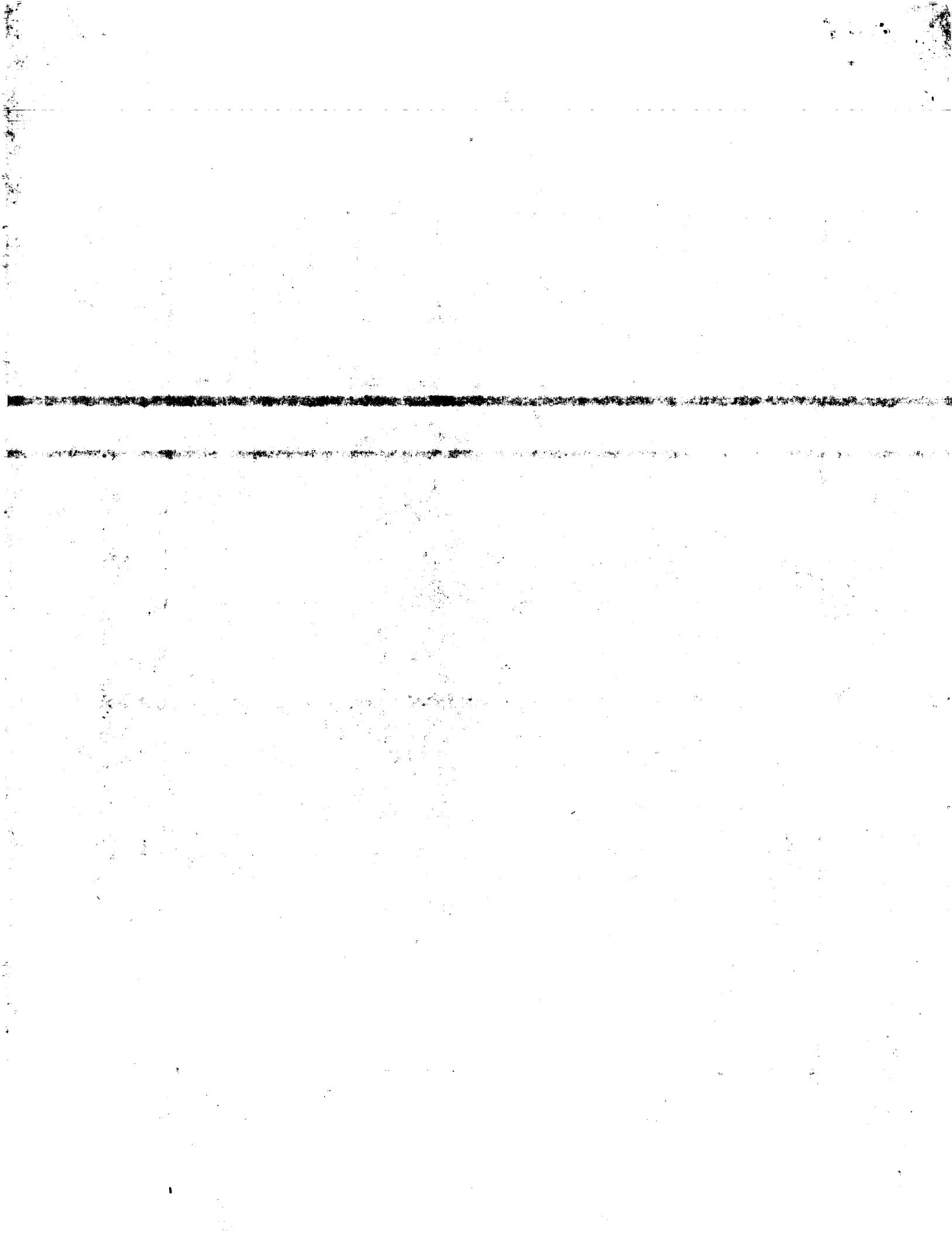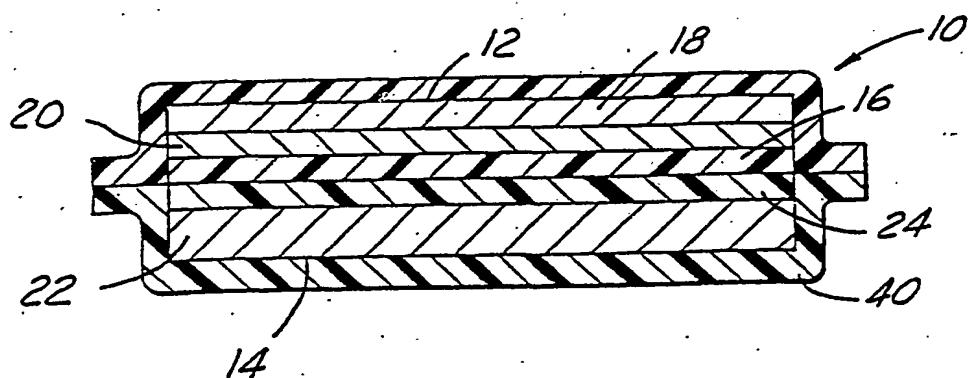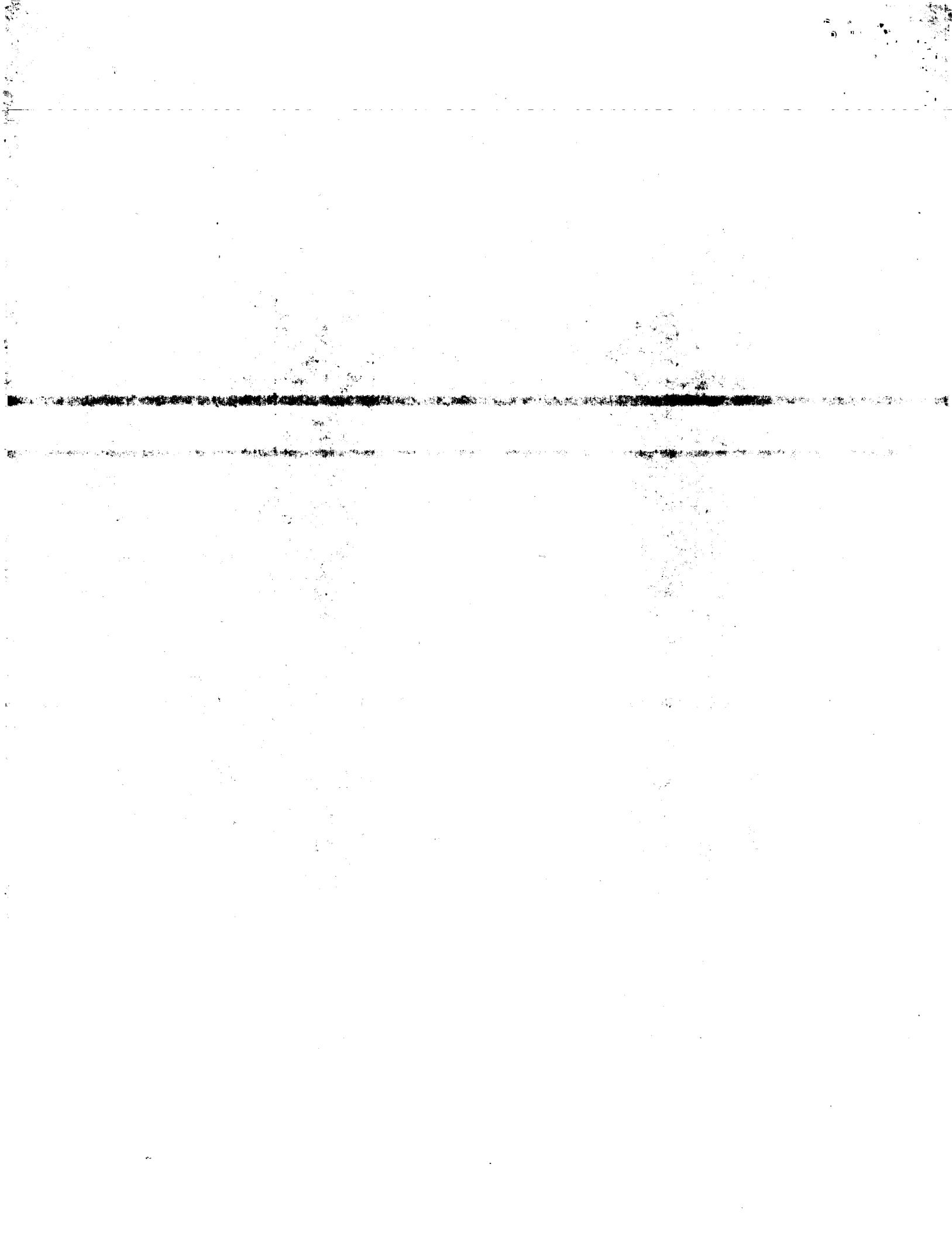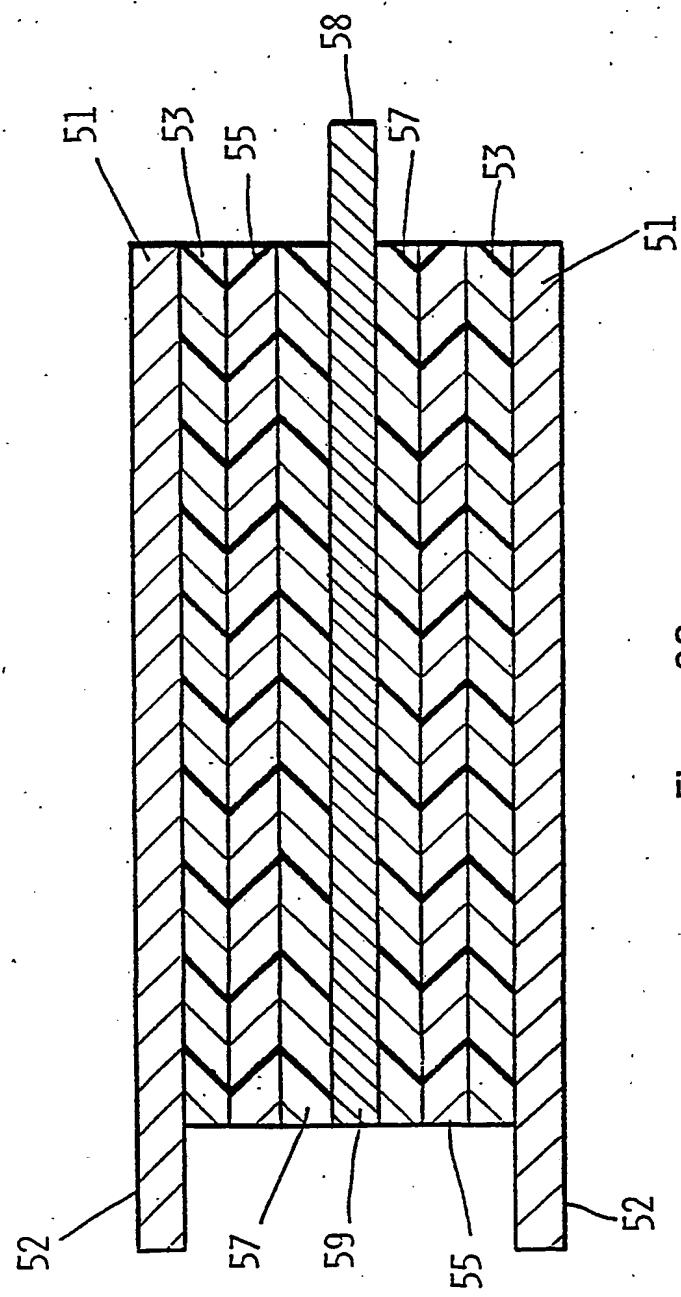
Figure 22

Figure 23
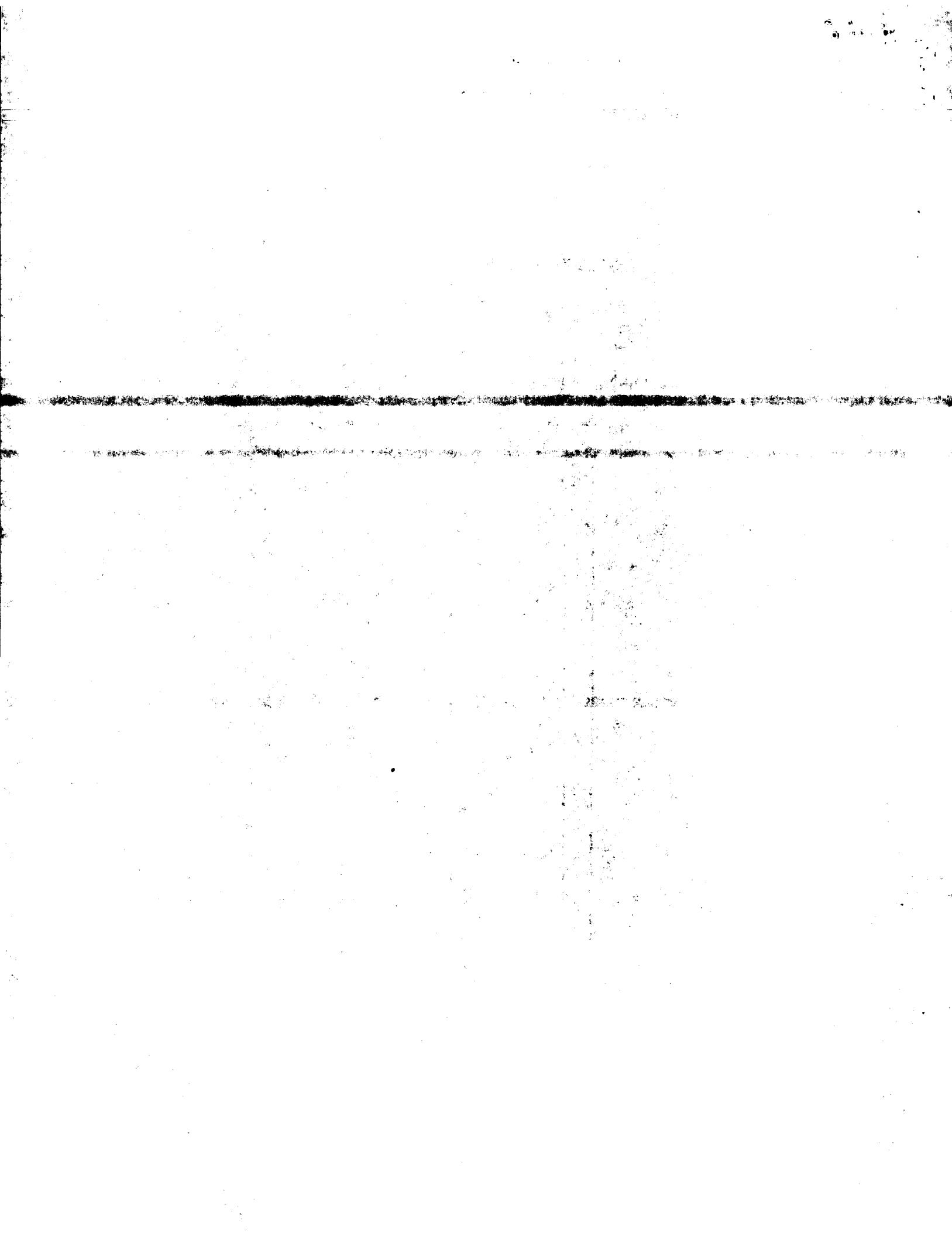
| | | lnternational Application No |
|---|---|---|
| | | PCT/US 00/35302 |

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7   H01M4/48       H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
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| [X] | Further documents are listed in the continuation of box C. | [X] | Patent family members are listed in annex. |
|---|---|---|---|

° Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 29 May 2001 | 0 8. 03.01 |

| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Authorized officer<br><br>Engl, H |
|---|---|

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 1999, no. 04,<br>30 April 1999 (1999-04-30)<br>& JP 11 025983 A (JAPAN STORAGE BATTERY CO<br>LTD), 29 January 1999 (1999-01-29)<br>abstract | 10-13,<br>23-25,<br>35-37 |
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-/--

# INTERNATIONAL SEARCH REPORT

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 5 567 548 A (WALK CHARLES R  ET AL)<br>22 October 1996 (1996-10-22)<br>column 4, line 3-59<br> claims | 31-41 |
| X | US 5 219 677 A (LABAT JEAN  ET AL)<br>15 June 1993 (1993-06-15)<br>column 5, line 37 -column 6, line 18<br> figures 6C-E | 38-41 |
| A | DELMAS C ET AL:  "THE LIXV2O5 SYSTEM: AN OVERVIEW OF THE STRUCTURE MODIFICATIONS INDUCED BY THE LITHIUM INTERCALATION"<br>SOLID STATE IONICS,NL,NORTH HOLLAND PUB. COMPANY. AMSTERDAM,<br>vol. 69, 1994, pages 257-264, XP002911464<br>ISSN: 0167-2738<br>the whole document | 38 |
| A | COCCIANTELLI J M ET AL:  "On the delta @rarr gamma irreversible transformation in Li//V2O5 secondary batteries"<br>SOLID STATE IONICS,NL,NORTH HOLLAND PUB. COMPANY. AMSTERDAM,<br>vol. 78, no. 1, 1 May 1995 (1995-05-01), pages 143-150, XP004050409<br>ISSN: 0167-2738<br>the whole document | 38-41 |

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/35302

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**Box I    Observations where certain claims wer  f  und unsearchable (C  ntinuati  n  f item 1  f first sheet)**

This International Search Report has not been established In respect of certaln claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the International Application that do not comply with the prescribed requirements to such
   an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

---

**Box II   Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

    see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all
   searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment
   of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report
   covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report Is
   restricted to the invention first mentioned In the claims; It Is covered by claims Nos.:

**Remark on Protest**          ☐ The additional search fees were accompanied by the applicant's protest.

                               ☒ No protest accompanied the payment of additional search fees.

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Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-37

    The compounds

    A    LiFe1-yMyPO4, where 0<y<0.5 and M = Mg, Ca, Zn, Sr,Pb, Cd, Sn, Ba, Be

    B    LiMI1-yMIIyPO4 where MI = Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr
            and MII = Mg, Ca, Zn, Sr, Pb, CD, Sn, Ba, Be

    C    LiMI1-yMIIyPO4 where MI is a transition metal from groups 4 - 11 in valence state +2 and MII is a metallic element selected form groups 1, 12 and 14 in valence state 2; and 0<y<1.

    Electrodes comprising said compounds, a binder and an electrically conductive carbonaceous material.

    Li ion batteries comprising said electrodes, a counterelectrode and an electrolyte.


2. Claims: 38-41

    A compound LiV2O5 with an orthorhombic crystal structure with a=9.7, b=3.6 and c=10.6 A.

    Electrodes comprising said compound, a binder and an electrically conductive carbonaceous material.

    Li ion batteries comprising said electrodes, a counterelectrode and an electrolyte.

| Patent document cited in search report | | Publication date | Patent family member(s) | | Publication date |
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